Vol. XIII No. 3
May - June 1958

JOURNAL OF ANALYTICAL CHEMISTRY of the USSR

ЖУРНАЛ АНАЛИТИЧЕСКОЙ ХИМИИ
(ZHURNAL ANALITICHESKOI KHIMII)

TRANSLATED FROM RUSSIAN

c/b CONSULTANTS BUREAU, NEW YORK

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CONSULTANTS BUREAU, INC.
227 W. 17th St., NEW YORK 11, N.Y.

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ANALYTICAL CHEMISTRY
OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
vol. 7, no. 1 Jan.-Feb. 1952

Annual subscription	*$80.00*
Single issue	*20.00*

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Printed in the United States

JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

V. I. Kuznetsov, Iu. A. Bankovskii and A. F. Ievin'sh

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The exceptional significance of dithizone, diethyldithiocarbamates, and other sulfur-containing reagents for analytical chemistry justifies the search for new sulfur-containing reagents. We have made a study of 8-mercaptoquinoline – the sulfur-containing analog of 8-hydroxyquinoline – as an analytical reagent. 8-Mercaptoquinoline has already been described long ago [1]; it has not yet been investigated as an analytical reagent, if one does not take into account one published article [2], the authors of which concluded that 8-mercaptoquinoline is of no interest from the viewpoint of analytical chemistry. 8-Mercaptoquinoline has attracted little attention from analysts, probably because of the difficultyof synthesizing it, and the poor keeping quality of its preparations which oxidize rapidly in the air. Since, however, one of us has developed a method of synthesizing 8-mercaptoquinoline [3], it has ceased to be available only with difficulty, while the discovery of the complete stability of the hydrochloride of 8-mercaptoquinoline in air has enabled 8-mercaptoquinoline to be kept in the form of this salt no less successfully than other sulfur-containing reagents.

On the basis of theoretical considerations advanced in [4], one can expect 8-mercaptoquinoline to exhibit the following properties:

a) This reagent should interact with elements of the hydrogen sulfide and ammonium sulfide groups, since the compounds formed by this reagent with the metals of these two groups contain a bond between the metal atom and sulfur, the tendency to whose formation is very characteristic for the elements of these two groups [4, 5].

b) 8-Mercaptoquinoline should react particularly energetically with those elements for which the existence of a clearly defined tendency to formation of stable sulfides and stable ammoniates is characteristic.

c) 8-Mercaptoquinoline should interact with the elements of the groups indicated, in more acid solutions than 8-hydroxyquinoline, since formation of sulfides proceeds in more acid solutions than formation of the hydroxides of these metals, the tendency to whose formation is reflected in the interaction of the elements with 8-hydroxyquinoline.

d) The complexes formed by 8-mercaptoquinoline, at least those complexes possessing normal composition, should be capable of extraction from aqueous suspensions by organic solvents which are immiscible with water. This should follow because of the binding (blocking) of the salt- and complex-forming groups of the molecules of 8-mercaptoquinoline by the atoms of the elements, since this blocking deprives the molecules of the reagent of their hydrophilic character and, in the absence of other interfering factors, enables the complex to be extracted completely [6].

e) 8-Mercaptoquinoline complexes should be colored. This follows from the fact that almost all compounds formed between metals and sulfur possess a chromophoric action and donate a color to those compounds into whose composition they enter [7]. In addition, these complexes contain the chromophoric combination Me – N.

By analogy with 8-hydroxyquinoline complexes, the possibility is not excluded in the case of 8-mercaptoquinoline complexes that the color intensity will increase as well, because of the presence of inner-molecular dissociation [8].

The study we have made of the analytical application of 8-mercaptoquinoline – preliminary results of which have been published earlier [9] – has shown that all the forecasts made above can be shown to be true. This clearly demonstrates once again the correctness of modern ideas regarding the mechanism of the reactions of organic reagents, and permits one with greater certainty on the basis of theoretical considerations, to indicate what will be the most interesting practical applications of any particular organic reagent. This facilitates experimental studies on the search for and study of new organic reagents.

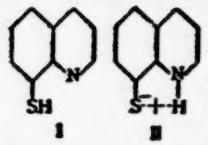
The Properties of 8-Mercaptoquinoline

Free 8-mercaptoquinoline (1) possesses totally different physical properties according to whether it contains water or is anhydrous.

Anhydrous 8-mercaptoquinoline C_9H_7NS is an intense blue colored liquid: on addition of water and, on even on storage in damp air, the material changes to a solid, red dihydrate. It is soluble in pyridine, quinoline, and ether, to give blue colored solutions, while in benzene and toluene the solutions are brown in color.

The reason for such a sharp difference between the colors of the anhydrous compound and the hydrate is not yet completely clear. The following is a possible explanation.

Many thioketo compounds containing aromatic nuclei are intensely colored. Thiobenzophenone [10], dithiobenzoic acid [11], and many of their analogs [12], just like anhydrous 8-mercaptoquinoline have a blue or blue-violet color. Since acid properties are fairly well pronounced in the thiophenols, free, anhydrous 8-mercaptoquinoline can be regarded as a partly inner-molecularly ionized compound (II). In this inner salt hydrogen is displaced toward the nitrogen, accordingly, the state of the sulfur approximates to its state in the intensely colored thioketo compounds. The blue color is the result.



I II

In the 8-mercaptoquinoline containing water, the groups $\backslash N =$ and $-SH$ are blocked by the connecting molecules of water and, accordingly, the state giving rise to the blue color does not develop. Formation of an inner salt can also be excluded by substitution of the hydrogen in the $-SH$ group by an alkyl group. Consequently S-ethyl-8-mercaptoquinoline is not blue but colorless.

In order to get inner complex salts of 8-mercaptoquinoline with a blue color, it would be necessary to have the salt of an element whose atom in the salt molecule would be strongly displaced toward the nitrogen atom and relatively far removed from the sulfur. In other words the element should possess a very strong tendency to form ammoniates and a relatively weak tendency to form sulfides. Ag, Cu, Ni, Zn, and the platinum metals form stable ammoniates. But Cu, Ag, and Zn to some extent, also form stable sulfides. This tendency is somewhat weaker in nickel and perhaps this is the reason the color of the nickel complex approximates to the color of anhydrous 8-mercaptoquinoline. The color of the nickel complex is not yellow like many other 8-mercaptoquinolates, but is raspberry.

The dihydrate $C_9H_7NS \cdot 2H_2O$ forms bright red needles, which on heating to about 58-59° split off water and change to the blue liquid, which was formerly taken to be the molten product [1].

In a vacuum, or on keeping in a desiccator over H_2SO_4, the elements of water are lost and the blue liquid is formed.

The solubility in 100 ml of water is 0.1 g (orange solution); the solubility in alcohol is about 12.5 g/100 ml (red solution). It dissolves in acids and alkalis to give yellow colored solutions.

In the solid state, and more rapidly in solution – particularly in alkalis – it is oxidized by atmospheric oxygen to the disulfide $C_9H_6NS \cdot SNC_9H_6$. It is stable in acid solutions.

The hydrochloride $C_9H_7NS \cdot HCl$ forms bright yellow crystals which are soluble in water, alcohol, and acetone acidified with hydrochloric acid, giving yellow colored solutions; it can be recrystallized from alcohol. It is insoluble in benzene. Both the solid material and its solutions are stable in air.

The sodium salt is fairly stable in the solid state in air but in aqueous solutions it is completely oxidized after a few days to the disulfide.

The disulfide of 8-mercaptoquinoline $C_9H_6NS \cdot SNC_9H_6$ is formed from 8-mercaptoquinoline by the action of an oxidizing agent, or by atmospheric oxygen in alkaline solutions; it is a bright yellow powder or crystals with a melting point of 206°. It is insoluble in water and alkalis, but dissolves in acids to give bright yellow colored solutions.

The analytical reactions of the disulfide are characterized by its capacity as a base to form sparingly soluble precipitates with a number of complex acids. Strong reducing agents (Ti^{III}, $Na_2S_2O_4$) change the disulfide to 8-mercaptoquinoline.

With solutions of the complex iodides of Bi, Sb, and Hg, the disulfide gives bright red precipitates, the formation of which is an interesting color reaction for these elements. Most of the other heavy anions form yellow precipitates.

The disulfide forms a dark brown precipitate with univalent copper, while with $SnCl_2$ it gives a yellow precipitate.

The Analytical Reactions of 8-Mercaptoquinoline

Precipitation of the Elements. The elements are precipitated by addition of an aqueous solution of 8-mercaptoquinoline hydrochloride to the test solutions; amorphous or granular precipitates are formed. By carrying out precipitation in a medium containing 30-40% of alcohol, many of the precipitates can be obtained in a crystalline form.

As a reagent forming the bond Me–S, 8-mercaptoquinoline precipitates elements of the hydrogen sulfide and ammonium sulfide groups, and particularly energetically precipitates elements which, in addition to forming Me–S bonds, also give stable bonds with amine nitrogen. Some elements are precipitated from solutions with a high acid content. The corresponding qualitative reactions are distinguished by high sensitivity.

8-Mercaptoquinoline, like 8-hydroxyquinoline, is a group reagent; this however does not prevent its use for carrying out various separations and determinations of different elements by adopting suitable conditions. The conditions and procedures followed in the case of these two reagents are, of course, different.

The new reagent, like 8-hydroxyquinoline, precipitates a number of elements in the form of compounds with a definite composition; and these compounds can, after drying, be weighed as such. Many of the compounds formed are readily soluble in organic solvents and can be extracted; this fact permits separation of insignificant amounts of certain elements from a large amount of other elements which do not react, and various separations can be carried out. In their capacity to be extracted by and to dissolve in organic solvents, the 8-mercaptoquinolates, in general, are better than the 8-hydroxyquinolates. Some 8-mercaptoquinolates in nonaqueous solutions form intensely colored solutions, so that photometric determinations become possible. With respect to the sensitivity of such reactions, 8-mercaptoquinoline is superior to 8-hydroxyquinoline and is similar to dithizone; 8-mercaptoquinoline, however, possesses better selectivity than dithizone.

By using 8-mercaptoquinoline, titrimetric determinations are also possible for a number of elements, which are based on the capacity of 8-mercaptoquinoline to change over smoothly into the disulfide under the action of an oxidizing agent.

8-Mercaptoquinoline differs from 8-hydroxyquinoline in that it exhibits a more clearly defined capacity to form sparingly soluble salts with acids which have heavy complex anions.

Some elements, depending on the conditions used, are capable of forming two different compounds. One compound is a typical inner-complex compound, while the other is the normal salt of the cation of 8-mercapto-

TABLE 1

Precipitation of Elements by 8-Mercaptoquinoline

Element	Conditions	Form and composition of the precipitate in the presence of excess reagent RH-C_9H_6NSH; R-C_9H_6NS	Notes
Ag	Acid medium	Bright red precipitate R–Ag · RH · · $3H_2O$	Formed, even in 24 N H_2SO_4
	" "	Yellow amorphous precipitate R–Ag	In the presence of excess Ag
	Ammoniacal	" "	
Cu^{II}	Acid, neutral, ammoniacal media	Brown precipitate $R_2Cu \cdot {}^1/_2H_2O$	Formed even in 4 N HCl and in 3 N NaOH
Au^{III}	Hydrochloric acid medium	Yellow crystalline precipitate $(RNHH)_3AuCl_6 \cdot H_2O$	
Zn	Acid, neutral, ammoniacal	Yellow amorphous precipate R_2Zn	
	Acid in the presence of SCN^-	Red precipitate $(RHH)_2 \cdot [Zn(SCN)_4]$	
Cd	Weakly acid, ammoniacal	Orange precipitate	In the presence of insufficient reagent – a yellow precipitate
Hg^{II}	Acid, neutral	Yellow amorphous precipitate R_2Hg	Formed even in 3 N HCl
Hg_2^{II}	Acid	Red-brown crystalline precipitate R–Hg · RH · $2H_2O$	
Tl^{I}, Tl^{III}	Weakly acetic	Yellow precipitate R–Tl	Tl^{III} reduced to Tl^{II}
Tl	Ammoniacal, alkaline	Yellow precipitate R–Tl	
Sn^{II}	Acid	Yellow amorphous precipitate	Composition variable
Sn^{IV}	Hydrochloric acid	Pale-yellow turbidity slowly develops	
Pb	Acid	Orange precipitate R_2Pb	
As^{III}	3 N HCl	Yellow crystalline precipitate $(RHH)_2AsCl_6 \cdot 3H_2O$	
As^{V}	Hydrochloric acid	Yellow crystalline precipitate R_5As	Soluble in concentrated HCl
Sb^{III}	Acid in the presence of tartrates	Yellow fine crystalline precipitate $R_3Sb \cdot H_2O$	
	Alkaline in the presence of tartrates	No precipitate	
	Strongly hydrochloric	Orange precipitate	Sb is precipitated as the anion
	Strongly hydrochloric in presence of I^-		
Sb^{V}	Hydrochloric acid	Yellow fine crystalline precipitate $(RHH)_3SbCl_6$	Sb^{V} converted to Sb^{III}
Bi	Alkaline in the presence of tartrates	Yellow amorphous precipitate R_3Bi	
V^{V}, V^{IV}	Acid	Light green precipitate R_2VO	V^{V} reduced to V^{IV}
Mo^{VI}	pH 2-3	Dark green precipitate $R_2MoO_2 \cdot H_2O$	
Mo^{VI}	Acid, on addition of $TiCl_3$	Light green precipitate	
W^{VI}	Acidification of alkaline solutions of tungstate-containing reagent	Dark green precipitate	
Mn^{II}	Alkaline in the presence of tartrates	Brown precipitate R_2Mn	
Fe^{III}, Fe^{II}	pH 5-6; alkaline in the presence of tartrates	Bright, red-brown precipitate $R_2Fe \cdot \cdot H_2O$	Fe^{III} reduced to Fe^{II}

TABLE 1 (continued)

Co^{II}	Weakly acid	Bright precipitate $R_2Co \cdot 2RH \cdot 2H_2O$
Ni	pH 6-6.5, ammoniacal	Bright raspberry, rapidly darkening precipitate $R_2Ni \cdot H_2O$
Pd	Strongly acid, neutral, alkaline	Red, fine crystalline precipitate $R_2Pd \cdot H_2O$

quinoline with the complex anion of the element. For example, in hydrochloric acid solution in the absence of thiocyanates, zinc gives yellow $(C_9H_6NS)_2Zn$, while in the presence of thiocyanates it gives a red precipitate of $(C_9H_6NSH_2)_2 \cdot [Zn(SCN)_4]$.

A drawback of 8-mercaptoquinoline is its tendency to be oxidized to the disulfide by atmospheric oxygen. All the same, in acid solutions, this process is so slow that it does not present any difficulties during the analytical application of the new reagent.

Details of the analytical application of 8-mercaptoquinoline for the determination of various elements will be given in subsequent articles. The present article only deals with its analytical reactions in the very broadest sense. The behavior of 8-mercaptoquinoline toward a series of elements under various conditions, the behavior, and appearance of the precipitates formed, are described in Table 1.

The Solubility of Precipitates in Organic Solvents. Bromobenzene, bromoform, benzene, and toluene are particularly good solvents for precipitates of the 8-mercaptoquinolates.

Precipitates formed by the following elements are readily soluble in organic solvents: Cu, Zn, Hg_2^{II}, Tl, Sn^{II}, Pb, As^{III}, As^{V}, Sb^{III}, Bi, V, Mo, Mn, Fe, Co, Ni, Pd.

Precipitates formed by Au, Cd, and W are less soluble; while the precipitates formed by Ag and Hg^{II} are soluble only in pyridine and quinoline.

All solutions in nonaqueous solvents are colored. The most intensely colored solutions (brown) are given by the precipitates formed by Mn, Fe, Cu, and Co; Mo (green) and Ni, Pd, Os, Pt (red) give less intensely colored solutions. A number of elements — Zn, Hg, Bi, Sb, As, Pb, and Tl — give relatively weak-yellow colored solutions.

Table 2 contains the values for the molar extinction coefficients of solutions of the 8-mercaptoquinolates of certain elements.

The capacity of many 8-mercaptoquinolates to be extracted is strongly dependent on the pH of the medium. The pH ranges within which complete extraction of the 8-mercaptoquinolates of individual elements is possible are given in Figs. 1 and 2, while in Fig. 3 is shown the position of the extracted elements in the Periodic System.

TABLE 2

Molar Extinction Coefficients of Solutions of Certain 8-Mercaptoquinolates (Room temperature)

Element	E_{mole}	λ_{max}, mμ	Solvent
Mn	7000	413	Chloroform
Pd	7750	485	"
Fe	7000	444	"
Cu	7530	431	"
V	7400	412	"

The Possible Analytical Applications of 8-Mercaptoquinoline. 8-Mercaptoquinoline permits determination of small amounts of elements. The reactions of 8-mercaptoquinoline supplement or, in some instances, successfully replace those given by dithizone. The fact that the capacity of certain 8-mercaptoquinolates to be extracted by a solvent is strongly dependent on the pH of the medium means that clear-cut extraction separation of a number of elements is possible. It is important to note that the extraction of a number of elements proceeds readily from solutions containing large amounts of energetic masking-complexing agents; this means that it should be possible to determine small amounts of certain elements on a background of large amounts of other elements. Thus, extraction of iron (II) at pH 6.5 is possible in the presence of very large amounts of tartrates, oxalates, citrates, phosphates, fluorides, and thiocyanates.

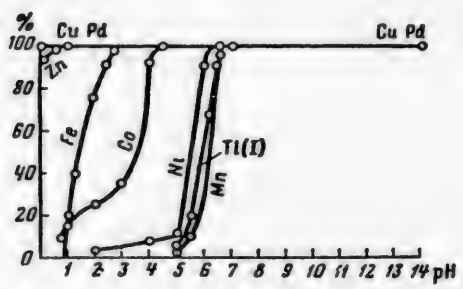


Fig. 1. Relation between the completeness of extraction of the 8-mercaptoquinolates of copper, palladium, zinc, iron, cobalt, nickel, thallium (I), and manganese, and the pH.

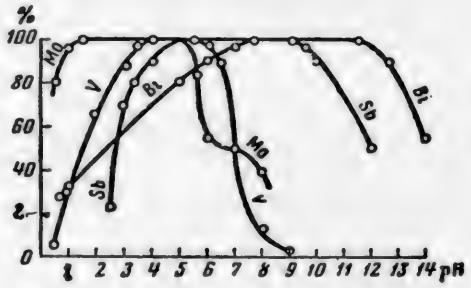


Fig. 2. Relation between the completeness of extraction of the 8-mercaptoquinolates of molybdenum, vanadium, antimony, and bismuth, and the pH.

Because of the intensity of the colors of the solutions of many of the metallic 8-mercaptoquinolates, direct photometric determinations of these elements is possible. The new reagent can, however, also be used for separation of elements with subsequent determination of individual elements by some other method; it is suitable as a component of organic coprecipitants and for amperometric titration.

H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	S	P	S	Cl	
K	Ca	Sc	Ti	(V)	Cr	Mn	(Fe) (C) (Ni)
[Cu]	[Zn]	[Ga]	Ge	(As)	(Se)	Br	
Rb	Sr	Y	Zr	Nb	[Mo]		[Ru] (Rh) [Pd]
[Ag]	[Cd]	[In]	[Sn]	(Sb)	(Te)	I	
Cs	Ba	La	Hf	Ta	[W]	Re	[Os] (Ir) [Pt]
[Au]	[Hg]	(Tl)	(Pb)	(Bi)	Po		
	Ra	Ac	Th	Pa	U		

Fig. 3. Extraction of elements by 8-mercaptoquinoline: □) extracted from strong acid solutions; O) extracted from weakly acid and neutral solutions.

8-Mercaptoquinoline can also find application for precipitating and extracting a series of elements from very acid solutions, a fact which may be significant in certain cases. In this connection, 8-mercaptoquinoline, from the point of view of convenience of application and the results obtained, is better than thionalide (β-naphthalide of thioglycolic acid).

The disulfide, which does not form inner-complex salts, is capable of being converted by reducing agents to the active 8-mercaptoquinoline, which means that it is possible to carry out a number of interesting analytical determinations in combination with reduction.

The stability of 8-mercaptoquinoline toward even the strongest reducing agents suggests that by making use of it, it should be possible to apply the complexes of the lower valency states of a number of elements (Mo, W, etc) for analytical purposes, something which is not possible when dithizone is used.

SUMMARY

Analytical reactions of 8-mercaptoquinoline are described which are useful for the extractive separation of elements, and for the extractive photometric determination of very small amounts of a number of elements. The sensitivity of the reactions given by this new reagent is similar to that for dithizone reactions. From the point of view of convenience of application, and analytical possibilities, 8-mercaptoquinoline has a number of advantages over dithizone and thionalide.

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Received March 28, 1957

• Original Russian pagination. See C.B. Translation.

PHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO IN THE PRESENCE OF ZIRCONIUM, TITANIUM, AND THE RARE EARTHS

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The reagent arsenazo (uranon, benzene-2-arsonic acid—⟨1-azo-7⟩ dihydroxynaphthalene-3,6-disulfonic acid), suggested by Kuznetsov [1], is more sensitive toward thorium than other azochromotropic dyes such as thoron [2], chromazurol [3], carmine red [4], morelline [5], naphthizarin [6], and quinalizarin [7], but its selectivity is low. Zirconium, titanium, the rare earths, and also sulfate, fluoride, and phosphate ions, oxidizing agents, and other materials interfere with the photometric determination of thorium with arsenazo [1]. This explains the slow introduction of arsenazo into the chemical practice of production laboratories.

In the work described here we tried to increase the selectivity of arsenazo for the photometric determination of thorium, and sought for ways of eliminating interference from zirconium, titanium, and the rare earths.

Relation between the Optical Density of the Complex formed between Thorium and Arsenazo, and the pH of the Solution and Concentration of the Reagent. Aqueous solutions of arsenazo in weakly acid media have a rose color which changes to violet in the presence of thorium.

In our experiments we used a solution of thorium nitrate containing 19.34 γ Th/ml, and a 0.05% solution of arsenazo. Into 8 standard flasks with a capacity of 25 ml was introduced the solution of thorium nitrate containing 57.68 γ of thorium; 2 ml of the 0.05% arsenazo solution was then added; this was followed by 5% hydrochloric acid, or 5% sodium acetate, in such amounts that the pH of the solution, after making up with water to the mark, was 0.5–3.5. The optical density of the solution formed was measured (in these and subsequent experiments) on a photocolorimeter, in a 20 mm cell, using a yellow-green filter (572 mμ). The results obtained showed (Fig. 1) that the optical density of the solution is highest at pH 1.3–3.0. The color of the thorium complex reaches its maximum intensity when the concentration of the reagent is 1–1.5 mg in 25 ml (Fig. 2).

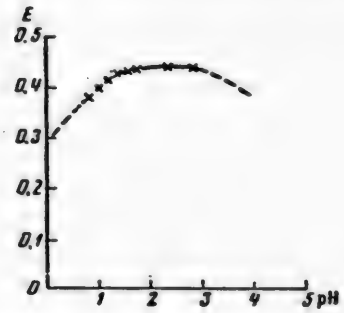

Fig. 1. Relation between the intensity of the color of the complex formed between arsenazo and thorium, and the pH.

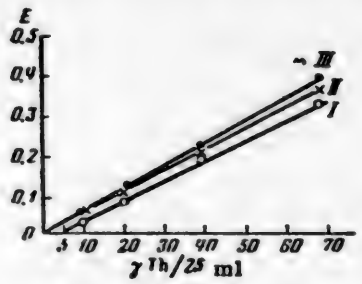

Fig. 2. Relation between the intensity of the color of the complex formed between arsenazo and thorium, and the amount of reagent: I) 0.25 mg arsenazo; II) 0.5 mg arsenazo; III) 1 and 15 mg arsenazo.

A Study of the Effect of Masking Agents on the Optical Density of Solutions of the Complexes formed between Arsenazo and Thorium and Zirconium. The color of solutions of the complex compound of zirconium with arsenazo is most intense at pH 1-2 [9]. The sensitivity of the reaction of thorium with arsenazo is equal to 0.7 γ/ml, while for zirconium it is about 0.1 γ/ml [9]. In the presence of even 5-10 γ of zirconium, determination of thorium is impossible.

Zirconium has a greater tendency to complex formation than thorium [8], and the complex compounds of zirconium are more stable than those of thorium. It is possible to choose compounds which would complex zirconium without touching thorium.

TABLE 1

Effect of Masking Agents on the Optical Density of Solutions of Complexes of Thorium and Zirconium with Arsenazo

5 mg of hydroxy acid added per 25 ml	Taken in, γ		Optical density	5 mg of hydroxy acid added per 25 ml	Taken in, γ		Optical density
	Th	Zn			Th	Zn	
	29	—	0.17	Sulfosalicylic			
Tartaric acid	29	—	0.17	acid	29	—	0.14
"	29	30	0.17	"	29	30	0.30
"	—	30	0.01	"	—	30	0.15
"	—	30	0.15	"	—	30	0.15
Citric acid	29	—	0.14	Ascorbic acid	29	30	0.17
"	29	30	0.15	"	29	30	0.30
"	—	30	0.00	"	—	30	0.15
"	—	30	0.15	"	—	30	0.15

Table 1 contains results on the effect of various hydroxy acids on the color of the complex compounds of thorium and zirconium with arsenazo.

Tartaric acid does not depress the optical density of the solution of the complex of thorium with arsenazo; zirconium does not give a color, while in the absence of tartaric acid, the optical density of the solution of the complex of zirconium with arsenazo is equal to 0.15. When citric acid is used, the optical density of solutions of the complex of thorium with arsenazo drops from 0.17 to 0.14, although the effect of zirconium on the optical density of the thorium complex is not noticeable; in the absence of citric acid, the intensity of the color of solutions of the zirconium complex is also equal to 0.15. Sulfosalicylic acid does not mask zirconium but decreases the color appreciably. Ascorbic acid does not affect the color of solutions of complexes of thorium and zirconium with arsenazo.

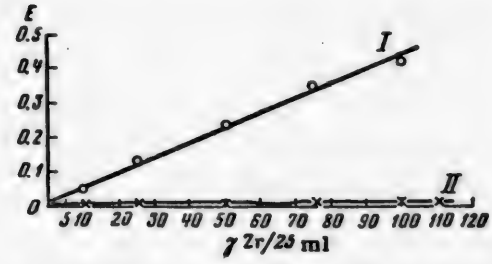

Fig. 3. Relation between the intensity of the color of the complex of zirconium with arsenazo, and the zirconium concentration: I) without tartaric acid; II) with tartaric acid; 5 mg in 25 ml.

Tartaric acid, as is evident from Table 1, eliminates interference from zirconium during the photometric determination of thorium by means of arsenazo.

It is clear from Fig. 3 that 5 mg of tartaric acid in 25 ml of solution completely suppresses the color of the complex of zirconium with arsenazo.

Table 2 contains results of measurements on the optical density of solutions of the complex of thorium with arsenazo, in the presence of various amounts of zirconium and tartaric acid.

From Table 2 it is clear that in the presence of 5 mg of tartaric acid in 25 ml of a solution containing 19.34 γ of thorium and up to 100 γ of zirconium, the optical density of the solution does not increase.

Zirconium, under the given conditions, does not interfere with the determination of thorium. In the presence of 10 mg tartaric acid, zirconium in amounts up to 150 γ does not interfere with the determination of thorium; when 30 mg of tartaric acid is used, zirconium does not interfere in amounts up to 300 γ; when 50 mg of tartaric acid is used, zirconium in amounts up to 700 γ (1:35) does not interfere with thorium determination. The optical density of solutions of the complex of thorium with arsenazo drops appreciably in the presence of 75-100 mg tartaric acid, so that determination of thorium is not feasible.

On the basis of these facts therefore, it is best to carry out determination of thorium by means of arsenazo in the presence of 50 mg tartaric acid in 25 ml of solution.

TABLE 2

Optical Density of Solutions of the Complex of Thorium with Arsenazo in the Presence of Zirconium and Tartaric Acid

Amount taken, in 25 ml			Optical density	Amount taken, in 25 ml			Optical density
$H_6C_4O_6$, in mg	Th γ	Zr γ		$H_6C_4O_6$, in mg	Th γ	Zr γ	
—	19.34	—	0.115	30.0	19.34	300	0.128
5.0	19.34	30.0	0.120	30.0	19.34	500	0.140
5.0	19.34	50.0	0.115	50.0	19.34	—	0.120
5.0	19.34	80.0	0.115	50.0	19.34	300.0	0.118
5.0	19.34	100.0	0.127	50.0	19.34	500.0	0.115
10.0	19.34	—	0.120	50.0	19.34	700.0	0.130
10.0	19.34	100.0	0.120	75.0	19.34	—	0.110
10.0	19.34	150.0	0.130	75.0	19.34	700.0	0.110
10.0	19.34	300.0	0.155	75.0	19.34	900.0	0.100
30.0	19.34	—	0.110	80.0	19.34	—	0.105
30.0	19.34	150	0.120	100.0	19.34	—	0.100
30.0	19.34	200	0.150				

Effect of Masking Agents on the Optical Density of Solutions of Thorium and Titanium Complexes with Arsenazo. Titanium, like zirconium, forms a colored complex with arsenazo and consequently interferes with the determination of thorium. The problem to be solved therefore was to eliminate interference from titanium during thorium determination. For this work a hydrochloric acid solution of titanium ($TiCl_6^{2-}$) was used; this solution was prepared as follows: 200 mg of titanium dioxide was fused in a porcelain crucible at 450-500° with 2.5 g of dry sodium peroxide. The cooled melt was dissolved in 200 ml of water and the whole boiled for 30 minutes. The solution was filtered and the precipitate on the filter washed 3-4 times with hot water; the titanium hydroxide was finally dissolved in 200 ml of hot 5% hydrochloric acid. Traces of hydrogen peroxide were removed by 1.0 N potassium permanganate. The titanium concentration was established by the cupferron method [10]. By diluting this stock solution with 5% hydrochloric acid, solutions of the requisite concentration were prepared.

Determination of thorium by means of arsenazo in the presence of titanium was studied using tartaric ($H_6C_4O_6$) and ascorbic ($C_6H_8O_6$) acids, as well as hydrogen peroxide.

Table 3 contains the results for determination of thorium in the presence of titanium, by means of arsenazo.

It is clear from Table 3 that up to 120 γ of titanium in 25 ml of solution does not affect the optical density of solutions of the complex of thorium with arsenazo. While the sensitivity of the reaction of thorium with arsenazo is equal to 0.07 γ/ml, that for titanium is only 5 γ/ml (i.e. 70 times less). The sensitivity of the reaction of titanium with arsenazo is even lower in the presence of 50 mg of tartaric acid; it is equal to 6 γ/ml. In the given instance, up to 150 γ titanium per 25 ml of solution (6 γ/ml) does not interfere during determination of thorium with arsenazo. Ascorbic acid also masks titanium; hydrogen peroxide depresses the optical density of solutions of the thorium arsenazo complex. Thus the use of tartaric and ascorbic acids ensures the photometric determination of thorium with arsenazo in the presence of considerable amounts of titanium (up to 8 γ/ml.)

TABLE 3

Effect of Titanium during Determination of Thorium with Arsenazo in the Presence of Complexing Agents

Am't contained in 25 ml sol'n			Optical density	Am't contained in 25 ml sol'n			Optical density
hydroxy acid in mg	Th γ	Ti γ		hydroxy acid in mg	Th γ	Ti γ	
—	19.34	—	0.165	$H_6C_4O_6$ 50	19.34	180.0	0.260
—	19.34	60.0	0.162	$C_6H_8O_6$ 10	19.34	180.0	0.165
—	19.34	120.0	0.160	$C_6H_8O_6$ 10	19.34	210.0	0.162
—	19.34	150.0	0.250	$C_6H_8O_6$ 10	19.34	240.0	0.300
$H_6C_4O_6$ 50	19.34	60.0	0.170	H_2O_2 30	19.34	—	0.140
$H_6C_4O_6$ 50	19.34	150.0	0.170	H_2O_2 30	19.34	60.0	0.140

Photometric Determination of Thorium in the Presence of the Rare Earths by Means of Arsenazo. The rare earths (total nitrates of the yttrium and cerium elements) in weakly acid or neutral media, just like thorium, form complex compounds of a blue-violet color with arsenazo [1]. The maximum color develops at pH 6-7; on decreasing the pH the color weakens and at pH 1-2 almost disappears.

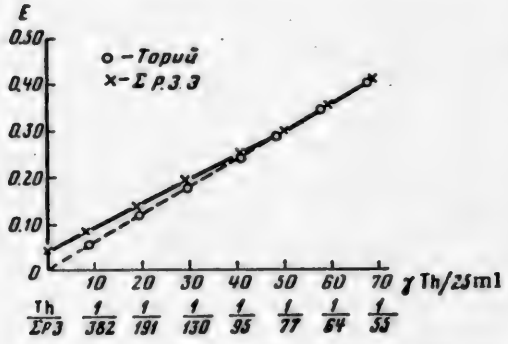

Fig. 4. Effect of the rare earths on the optical density of solutions of the complex of thorium with arsenazo (pH 1.3): O) Thorium; x) rare-earths

It is evident from Fig. 4 that at a ratio of thorium to the rare earths of 1 : 95 at a pH of 1.3, no deviation of the curve from the normal position (denoted by the dotted line) is observed. At higher ratios of the rare earths to thorium, the optical density of the solution decreases. When cerium is present it should be reduced to the trivalent state before carrying out photometric determinations of thorium with arsenazo. Ascorbic acid reduced Ce^{IV} to Ce^{III} in weakly acid media.

Tartaric acid in amounts of 50 mg per 25 ml of solution was also used in the next series of experiments as a masking agent.

Results for thorium determination in presence of various amounts of the rare earths are given in Table 4.

It follows from Table 4 that the rare earths, when present in amounts which are 900 times that of thorium, do not interfere with the photometric determination of the latter. In practice thorium could be determined at any concentration of the rare earths.

A Method for the Determination of Thorium in the Presence of Zirconium, Titanium, and the Rare Earths

An aliquot of the oxides of thorium, zirconium, titanium, and the rare earths* equal to 20-25 mg, is placed in a small porcelain crucible (1.5-2 ml), to which 0.2-0.3 g of dry sodium peroxide has been added beforehand. The aliquot is covered with 0.8-1.0 g of sodium peroxide and the mixture fused until a homogeneous melt is obtained; the crucible is cooled and transferred to a 100-ml beaker, 50-60 ml of water is added and the whole heated for 10-15 minutes. The crucible is withdrawn from the beaker and the solution filtered through a filter paper (white ribbon grade 6 cm). The hydroxides on the filter paper are washed 5-6 times with hot water; the filtrate and washings are discarded.

* They are freed from the major amounts of titanium and zirconium by the oxalate method. Thorium, rare earths, and calcium are quantitatively removed as the oxalates when calcium is used as the collector. The oxalates may contain traces of zirconium and titanium.

TABLE 4

Determination of Thorium with Arsenazo in the Presence of the Rare Earths

Hydroxy acid in 25 ml, in mg	Amount taken		Th : Σ rare earths	Optical density	Th found, in γ
	Th γ	Σ rare earths, mg			
—	—	25	—	0.05	—
—	—	10	—	0.04	—
—	—	5	—	0.02	—
—	—	3	—	0.01	—
Tartaric acid 50 mg, ascorbic acid 10 mg	—	25	—	—	—
The same	29.00	4	1 : 150	0.170	29.0
"	29.00	8	1 : 250	0.165	28.5
"	29.00	10	1 : 300	0.165	28.5
"	29.00	20	1 : 700	0.170	29.0
"	29.00	25	1 : 900	0.165	28.5
"	9.67	3	1 : 300	0.060	9.5
"	9.67	5	1 : 520	0.060	9.5
"	19.34	5	1 : 250	0.110	18.5
"	19.34	10	1 : 520	0.120	19.5
"	9.67	—	—	0.060	9.5
"	19.34	—	—	0.110	18.5
"	29.00	—	—	0.170	29.0

The stem of the funnel containing the filter paper is inserted into a 25-50-ml standard flask; the hydroxides on the filter paper are dissolved in 5-10 ml of 5% hot (80-90°) hydrochloric acid, ammonia is then added dropwise until the hydroxides are precipitated. The hydroxides are dissolved in 2-3 drops of hydrochloric acid

TABLE 5

Determination of Thorium by Means of Arsenazo in the Presence of Zirconium, Titanium, and the Rare Earths

Amount taken, in mg				Th found, in mg	Error in Th, in mg
Th	Zr	Ti	Σ rare earths		
0.006	0.080	—	10.0	0.005	−0.001
0.006	—	—	10.0	0.005	−0.001
0.006	0.080	—	10.0	0.006	0.000
0.019	0.200	0.060	20.0	0.019	0.000
0.019	0.200	0.090	20.0	0.019	0.000
0.019	0.200	0.120	20.0	0.020	+0.001
0.019	0.200	0.150	20.0	0.018	−0.001
0.019	0.200	0.180	20.0	0.019	0.000
0.019	0.200	0.210	20.0	0.020	+0.001
0.055	0.200	—	20.0	0.049	−0.006
0.055	0.200	—	20.0	0.060	+0.005
0.055	0.200	—	20.0	0.050	−0.005
0.110	0.300	—	20.0	0.115	+0.005
0.110	0.300	—	20.0	0.113	+0.003
0.110	0.300	—	20.0	0.112	+0.002
0.110	0.300	—	20.0	0.110	0.000
0.170	2.500	—	100.0	0.160	−0.010
0.170	2.500	—	100.0	0.170	0.000

sp. gr. 1.12, and the filter paper is washed with 0.09 N hot hydrochloric acid until the amount of solution in the flask is about 20-40 ml respectively (according to whether a 25 or 50-ml flask is used in the first instance).

1-2 ml of 1% ascorbic acid is added to the cooled solution and the whole thoroughly mixed. The solution is made up to the mark with 0.09 N hydrochloric acid, the whole mixed again, and the thorium determined.

For this purpose 5-20 ml of the test solution is measured into a 25-ml standard flask, 0.5 ml of 10% tartaric acid, and 3 ml of 0.05% arsenazo solution are then added, the volume is made up to the mark with 0.09 N hydrochloric acid and the solution mixed thoroughly. The optical density is measured on a photocolorimeter using a yellow-green filter (570-572 mμ) and 30 mm cells.

The amount of thorium is established by means of a calibration curve. The blank solution is an aqueous solution of arsenazo containing 3 ml of 0.05% arsenazo to 25 ml of 0.09 N hydrochloric acid.

It is clear from Table 5 that results for the determination of thorium in the presence of zirconium, titanium, and the rare earths are satisfactory.

SUMMARY

It has been established that interference from zirconium, titanium, and the rare earths during the photometric determination of thorium with arsenazo can be eliminated by means of tartaric acid. A method has been developed for the determination of thorium by means of arsenazo in the presence of the elements indicated.

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Received February 9, 1957

*Original Russian pagination. See C.B. Translation.

REMOVAL OF ETHYLENEDIAMINETETRACETIC ACID FROM SOLUTION BY OXIDATION

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Ethylenediaminetetracetic acid (Complexon II) and its disodium salt (Complexon III) are finding more and more applications in analytical chemistry and chemical industry [1-17].

When analyses are carried out, the need sometimes arises for removing the complexons from the test solution; for this purpose oxidative breakdown is the most convenient. The study of the oxidation of complexons is also of interest because of the possibility of the presence of oxidizing agents in certain test solutions.

Only the breakdown of ethylenediaminetetracetic acid by heating with chlorates in hydrochloric acid media is described in the literature [18]. There is a reference to the interaction of ethylenediaminetetracetic acid with hydrogen peroxide in the cold [19]. The considerable stability of the complexons to nitric acid has been noted in a number of papers, but quantitative data is not adduced.

We have studied the oxidation of ethylenediaminetetracetic acid by nitric acid, nitrous acid, and ammonium persulfate.

1. Preparation of Solutions. An aqueous solution of diammonium ethylenediaminetetracetate containing 100 mg/ml was prepared by dissolving the requisite amount of Complexon II purified by the method of Blaedel and Knight [20] in ammonia. The solution thus prepared was standardized by complexometric titration with standard magnesium sulfate, using chromogen black special, ET-00 (eriochrome black T) in the form of finely ground powder mixed with NaCl in the ratio 1 : 200 as indicator.

The ammoniacal buffer solution with pH about 10 was prepared by dissolving 70 g of NH_4Cl in 500 ml ammonia (d = 0.9) and diluting this solution to 1000 ml.

Only chemically pure grade chemicals were used for the work. All the solutions were made up in distilled water which had been passed through the cation exchange resin KU-2 in the sodium form.

The vessels used for the work were boiled in a 2% ammoniacal solution of Complexon II in order to avoid errors connected with washing out of cations from the glass [21].

2. Experimental Procedure. To a measured volume of Complexon II solution acidified with HNO_3 and contained in a 250-ml conical flask was added the oxidizing agent, and the volume of the solution made up to 100 ml.

The flask was fitted with a reflux condenser to avoid changes in volume during heating. 25-ml aliquots were taken from the solution and transferred to 250-ml conical flasks, the aliquots were then diluted to about 100 ml and the excess acid titrated with 2 N KOH using congo red as indicator. 2-3 ml of buffer solution was added to each aliquot, indicator was next added until a clear-cut blue color was obtained; the solution was finally titrated with 0.01 M $MgSO_4$ until the color started to change to red-violet. From the amount of $MgSO_4$ solution used up in the titration, the percentage decomposition of Complexon II was calculated.

EXPERIMENTAL RESULTS AND DISCUSSION

a) Oxidation of Complexon II by Nitric Acid. As the results given in Table 1 show, Complexon II is oxidized very slowly in the cold by nitric acid. Percentage breakdown increases with increasing contact

time and acid concentration, and reaches an appreciable value (about 4%) on long contact with 4 N HNO_3.

In neutral media, without heating, the titer of the Complexon II solution did not change even in the presence of large amounts KNO_3.

TABLE 1

Oxidation of Complexon II (4 mg/ml) by Nitric Acid at Room Temperature

HNO_3 concentration, in mole/liter	Contact time, in hours	Oxidation of Complexon II, in %	HNO_3 concentration, in mole/liter	Contact time, in hours	Oxidation of Complexon II, in %
0.5	24	0.0	2.0	24	0.4
0.5	48	0.1	2.0	48	0.6
0.5	192	0.8	2.0	192	2.2
1.0	48	0.4	4.0	24	0.7
1.0	96	0.7	4.0	48	1.1
1.0	192	1.3	4.0	192	4.0

On boiling nitric acid solutions of Complexon II, oxidation speeds up considerably (Table 2), nevertheless, complete breakdown is not achieved even on prolonged boiling with 4 N HNO_3. In neutral solutions in the presence of KNO_3, Complexon II is oxidized very slowly on boiling.

Accordingly, nitric acid is not suitable for the quantitative removal of Complexon II. During complexometric titration even of hot solutions, the nitrate ion does not interfere, since titration is carried out rapidly and at low acidity (pH 1.7-13).

TABLE 2

Oxidation of Complexon II (4 mg/ml) by Nitric Acid on Boiling

Duration of boiling, in hours	HNO_3 concentration, in mole/liter	Breakdown of Complexon II, in %	Duration of boiling, in hours	HNO_3 concentration, in mole/liter	Breakdown of Complexon II, in %
0.5	0.5	2	0.5	2.0	11
1.0	0.5	4	1.0	2.0	17
2.0	0.5	7	2.0	2.0	37
4.0	0.5	15	4.0	2.0	50
0.5	1.0	6	0.5	4.0	14
1.0	1.0	11	1.0	4.0	18
2.0	1.0	20	2.0	4.0	34
4.0	1.0	28	4.0	4.0	63

b) Oxidation of Complexon II by Nitrous Acid. Nitrous acid oxidizes ethylenediaminetetracetic acid more actively than nitric acid. Table 3 contains the results of tests on the oxidation of a 0.4% solution of Complexon II during a 30-minute boil in 0.5 HNO_3 to which various amounts of $NaNO_2$ had been added.

With increasing amounts of sodium nitrite, initially there occurs an increase in the percentage oxidation of Complexon II, nevertheless, further increases in the amounts of nitrite have no effect on completeness of the oxidation. Increasing boiling time and the HNO_3 concentration do not lead to a 100% oxidation of Complexon II either. This can be explained by the rapid breakdown of sodium nitrite with liberation of nitrogen oxides. Consequently, in subsequent experiments, addition of $NaNO_2$ was continued in 1 g or 0.5 g portions

per 100 ml of a 0.4% solution of Complexon II in 0.5 N HNO_3 every 30 or 60 minutes boiling time (Table 4).

In this way, by adding $NaNO_2$ in portions it is possible by boiling for 3 hours to achieve complete oxidation of ethylenediaminetetracetic acid. The concentration of the ethylenediaminetetracetic acid does not affect its oxidation by nitrous acid. Additions of 6 separate portions of 750 mg of $NaNO_2$ per 100 mg Complexon II (in the course of 3 hours at the boiling point) lead to complete breakdown of the complexon.

TABLE 3

Oxidation of Complexcn II by Sodium Nitrite

Amount of $NaNO_2$, in g	Percentage breakdown of Complexon II, in %
0.2	35
0.5	46
1.0	60
2.0	60
4.0	60

c) Oxidation of Complexon II by Ammonium Persulfate. Complexon II is oxidized very rapidly by ammonium persulfate in a weakly acid medium at the boiling point. Complete oxidation of 100 mg of Complexon II is achieved by adding 200 mg of $(NH_4)_2S_2O_8$ and boiling for 10-15 minutes; changes in acid concentration ranging from 0.1 N to 2 moles/liter do not appreciably affect oxidation of the complexon. Complexon II concentration has no effect either.

For the rapid and complete breakdown of Complexon II therefore the following technique can be recommended.

To a solution of Complexon II acidified with HNO_3 is added an excess of ammonium persulfate (not less than twice the amount of the Complexon II in solution); the solution is heated to the boil and the temperature kept at this point for 10 minutes.

A drawback of this procedure is the formation of SO_4^{2-}, which sometimes interferes with the subsequent course of the analysis. In such cases another technique can be used.

To a nitric acid solution (0.5-1 N), sodium nitrite is added in small portions while the solution is being boiled. The amount of $NaNO_2$ added should be about 10 times the amount of Complexon II is solution.

TABLE 4

Oxidation of Complexon II on Addition of $NaNO_2$ in Portions

Duration of boiling, in min	Am't of $NaNO_2$ added, in g	Number of portions	Oxidation of Complexon II, in %
60	1.0	1	60
120	1.0	2	85
180	1.0	3	99.5
240	1.0	4	100
30	0.5	1	45
60	0.5	2	90
120	0.5	4	97.5
180	0.5	6	100

SUMMARY

The percentage oxidation of Complexon II by nitric acid, nitrous acid, and ammonium persulfate has been studied. A technique has been developed for the rapid breakdown of Complexon II by ammonium persulfate and sodium nitrite.

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Received February 12, 1957

POLAROGRAPHIC CHARACTERISTICS OF THE THIOSEMICARBAZIDE COMPLEX OF COPPER IN SULFURIC AND HYDROCHLORIC SOLUTIONS

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The polarographic method has been successfully used for studying the complex compounds of many cations [1]. The chief condition for the applicability of the polarographic method for the determination of the instability constants of complexes [2] is the reversibility of the reduction of the ions on a dropping mercury cathode.

Every reversible electrode process is characterized by the fact that its only slow stage is the slow diffusion of ions to the electrode surface. The other stages of the electrode process are fairly rapid. The value of the electrode potential depends on the concentration of the ions located near the electrode surface.

The equation for the cathode wave in the case of reversible processes is of the following form:

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i}.$$

In the case of irreversible electrode processes, the shift in potential of the half-wave is not directly related to the instability constant of the complex. This shift depends on the value of the exchange current and the discharge and ionization constants (α and β) [3]. Moreover, complexes with a different composition than those found in solution in the greatest amounts may be discharged.

The solutions were examined polarographically on a visual polarograph of the UFAN type (Ural Branch of the USSR Academy of Sciences). A saturated calomel electrode was used as the anode, this being connected to the electrolyzer via an agar-agar bridge with saturated potassium chloride. The cathode was a dropping mercury electrode. The dropping time was determined from the time of formation of a drop at the half-wave potential, for a constant value of the mercury column (τ = 1.01 seconds).

The value of m for the capillary was 1.57 mg/second. The capillary used had the following characteristic:

$$m^{2/3} \tau^{1/6} = 1.35 \text{ mg}^{2/3} \text{ second}^{-1/2}.$$

A mirror galvanometer with the following characteristics was used for measuring the current passing through the electrolyzer: R_{EN} = 398 ohm; $R_{crit.}$ = 1312 ohm. The oscillation period of the mirror was 16 seconds, and the sensitivity of 0.97×10^{-9} amperes/mm/m. All tests were carried out in a thermostat at a temperature of 25 ± 0.3°.

The solutions used were prepared from twice-distilled water. Cupric sulfate, potassium chloride, and thiosemicarbazide were twice recrystallized from the twice-distilled water.

The solution of thiosemicarbazide sulfate was prepared by dissolving an aliquot of the material in 2 N sulfuric acid, while that of the thiosemicarbazide chloride was prepared using 1 N hydrochloric acid. The copper concentration was 4×10^{-4} mole/liter, while that of the sulfate and chloride of thiosemicarbazide was $4 \times 10^{-3} - 4 \times 10^{-2}$ mole/liter.

The pH value – measured potentiometrically by means of a quinhydrone electrode – was equal to one for sulfuric acid solutions of copper thiosemicarbazide, and to zero for hydrochloric acid solutions.

Dissolved oxygen was removed from solution by passing hydrogen for 10-15 minutes through the solution; polarograms were then taken.

Corrections for the ohmic drop in the electrolyzer circuit were applied during determination of $E_{1/2}$.

The resistance of the electrolyzer we used had a value of 550-650 ohms. For a current strength of 10-20 μA, the correction for the ohmic drop in the electrolyzer circuit did not exceed 0.0065-0.0116 volt.

The polarographic wave for reduction of thallium ions on a dropping mercury electrode in a supporting electrolyte of 1 N KOH was taken first. The half-wave potential in the given case, according to [2], is equal to 0.475 volt. The value we obtained for the half-wave potential during reduction of thallium ions almost agreed with this, and was found to lie within the limits 0.476-0.481 volt.

In order to check on the reversibility of the reduction of copper thiosemicarbazide complex, the cathodic wave in a solution containing 4×10^{-4} mole/liter of Cu^{2+} in a supporting electrolyte of 2 N sulfuric acid (activity about 1) was taken. It is clear from Fig. 1 that reduction of cupric ions on a dropping mercury electrode using 2 N H_2SO_4 as supporting electrolyte proceeds in one stage: $Cu^{2+} + 2e \rightarrow Cu^0$.

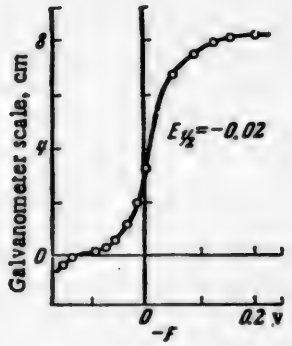

Fig. 1. Polarogram for a solution of cupric sulfate in 2 N sulfuric acid.

Polarograms were then taken for solutions containing cupric sulfate (4×10^{-4} mole/liter) and thiosemicarbazide. In Figs. 2a and 3 are shown the cathodic waves for reduction of the copper thiosemicarbazide complex.

The addition of thiosemicarbazide to the solution leads to a shift of the half-wave potential toward negative values (Figs. 2a and 3); this last fact indicates that a complex is formed between copper and thiosemicarbazide. The value of the half-wave potential for reduction of the copper thiosemicarbazide complex in a supporting electrolyte of 2 N sulfuric acid is -0.35 to -0.31 volt.

The curve in Fig. 2b, drawn within the coordinates E – logarithm $\frac{i}{i_d - i}$, testifies to the fact that one of the chief conditions for the reversibility of a given electrode process is not observed.

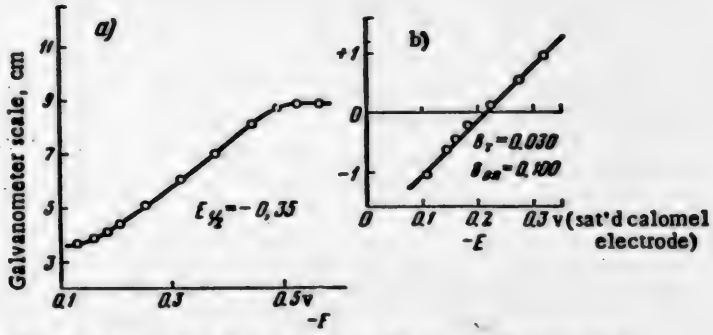

Fig. 2. Polarogram for a solution of the copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte. Concentration of the thiosemicarbazide added 4.0×10^{-3} mole/liter.

The value of the tangent (for a copper concentration of 4×10^{-4} mole/liter and thiosemicarbazide concentration of 4×10^{-3} mole/liter) as found by calculation on the basis of several experiments ($volt_{expt.}$) proved to be 0.100, while the theoretical value of this coefficient ($volt_{theor.}$) corresponding to a reduction of Cu^{2+} to Cu^{0} is equal to 0.030.

Moreover, on increasing the thiosemicarbazide concentration 10 times (from 4×10^{-3} to 4×10^{-2} mole/liter), the half-wave potential of the copper complex shifts by 0.04 volt to more positive potential, from -0.35 to -0.31 volt. It is easy to see that if the process were reversible, this shift should be toward the negative side.

On this basis, it is possible to conclude that reduction of the copper thiosemicarbazide complex in sulfuric acid solutions belongs to the category of irreversible electrode processes and, consequently, it is impossible to determine the instability constant of the copper thiosemicarbazide complex polarographically.

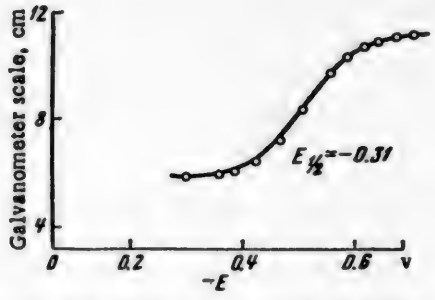

Fig. 3. Polarogram for a solution of copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte. Thiosemicarbazide concentration 4.0×10^{-2} mole/liter.

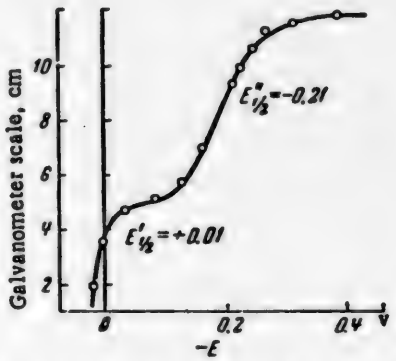

Fig. 4. Polarogram for a solution of cupric sulfate in 1 N hydrochloric acid as supporting electrolyte.

For the polarographic study of the copper thiosemicarbazide complex in a supporting electrolyte of hydrochloric acid, cathodic waves for Cu^{2+} in hydrochloric acid with an activity of about 1 (Fig. 4.) were again taken first; the solution contained 4×10^{-4} mole liter of copper. In this case, two waves were observed, one with a half-wave potential of +0.01 volt and the other with a half-wave potential of -0.21 volt; this is in accordance with published results: +0.04 volt and -0.22 volt for 1 M HCl (KCl) [4]. Cathodic waves were then taken for solutions containing cupric ions 4×10^{-4} mole/liter, and thiosemicarbazide $4 \times 10^{-3} - 4 \times 10^{-2}$ mole/liter in a supporting electrolyte of 1.0 N hydrochloric acid. The nature of the reduction of the complex ions of divalent copper in a hydrochloric acid solution of thiosemicarbazide can be followed by means of Figs. 5 and 6. It is clear from these diagrams that the discharge of the complex copper ions proceeds in two stages. The half-wave potential of the cathodic wave corresponding to the first stage of the discharge of the copper thiosemicarbazide complex shifts by 0.03 volt toward negative values, while the half-wave potential of the second stage shifts by 0.07 volt. It follows, therefore, that in a hydrochloric acid solution of thiosemicarbazide, complex copper ions are formed.

It is clear from Fig. 5 that the values of the half-wave potentials corresponding to reduction of the copper thiosemicarbazide complex in 1 N hydrochloric acid are equal to -0.02 and -0.28 volt.

A consideration of the curve constructed within the coordinates

$$E - \text{logarithm} \frac{i}{i_d - i}$$

(Fig. 5b) shows that the value of the tangent $v_{expt.}$ of the second stage of the discharge is equal to 0.100; it

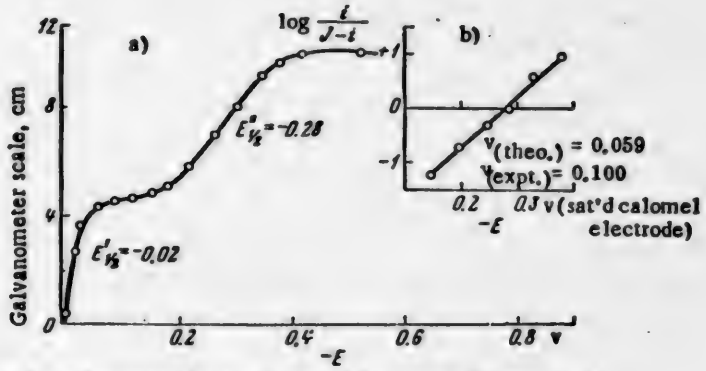

Fig. 5. Polarogram for a solution of the copper thiosemicarbazide complex in a supporting electrolyte of 1 N hydrochloric acid. Thiosemicarbazide concentration 4.0×10^{-3} mole/liter.

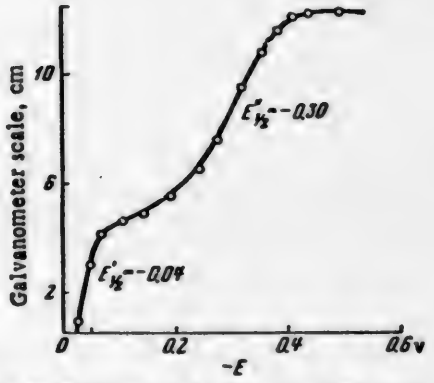

Fig. 6. Polarogram for the copper thiosemicarbazide complex in 1 N hydrochloric acid as supporting electrolyte. Thiosemicarbazide concentration 4.0×10^{-3} mole/liter.

is about one and a half times the theoretical value $v_{theor.}$ (0.059 at 25°); the process is accordingly irreversible. The tangent for the first stage of the discharge of the complex could not be calculated because it was impossible to determine the height of the first wave (i_d).

Preliminary experiments have shown that it is possible to determine copper polarographically in the form of its thiosemicarbazide complex.

We should like to thank A. G. Stromberg for his valuable advice.

SUMMARY

1. It has been established that the value of the half-wave potential for the cathodic reduction of the copper thiosemicarbazide complex in 2 N sulfuric acid as supporting electrolyte is equal to -0.31 to -0.35 volt (with respect to the saturated calomel electrode).

2. It has also been established that the values of the half-wave potential for the cathodic reduction of the copper thiosemicarbazide complex in 1 N hydrochloric acid as supporting electrolyte are 0.02-0.04 volt

and -0.28 to -0.30 volt, respectively, for the first and second stages.

3. It has been shown that reduction of the copper thiosemicarbazide complex on a dropping mercury electrode is irreversible in both sulfuric and hydrochloric acid as supporting electrolyte.

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Received August 6, 1956

HIGH-FREQUENCY TITRATION

COMMUNICATION IV. AN APPARATUS BASED ON A BRIDGE SETUP*

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The successful penetration of high-frequency alternating currents into chemical analysis and production control will be determined above all by whether or not the apparatus used is readily portable, simple in construction, and sensitive to concentration changes over a wide range of concentrations. The present article contains a description of an apparatus which will satisfy these requirements to a greater extent than the setup described by us previously [1, 2].

1. Block Diagram of the Apparatus. When a cell for high-frequency titration is included in one of the arms of an ac measuring bridge, it is practically impossible to get a definite zero during balancing. This is explained by the appearance in the arms of the bridge of a shift in the voltage phase, and the appearance of additional harmonics (clear-factor) on the ends of the measuring diagonal. Complete elimination of these additional harmonics would complicate the setup considerably, since during balancing of the bridge it would be necessary to equate the voltage with respect to its modulus and phase simultaneously.** Accordingly, an ac bridge has not hitherto found application for high-frequency titration, and has only been partly used for measuring the concentrations of solutions over a narrow range of concentration changes with the help of calibration curves.

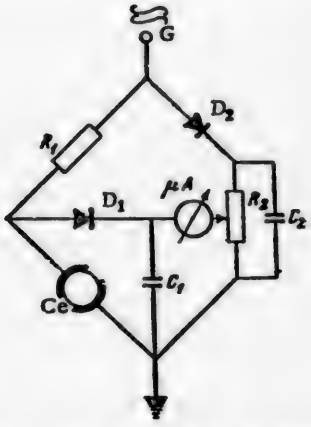

Fig. 1. Block diagram of the apparatus: G) high-frequency generator (35 megacycles; D_1, D_2) germanium detector DGTs 6; Ce) titration cell; μA) microammeter.

The bridge which we suggest in the present article is free from these drawbacks. In the apparatus described below, a high-frequency voltage is applied to the bridge, while the bridge is balanced on the basis of a dc current. Actually, as is clear from the block diagram, one of the branches of the bridge contains two resistances connected in series — an active resistance R_1 and the total resistance of the cell "Ce," while at the point where they join, a diode D_1 is applied; this diode rectifies the voltage across the cell. This rectified voltage is compensated by a constant voltage obtained by including a second

*For Communication III see [11].

**For equilibrium of an ac bridge the following equation holds (in a complex form):

$$z_1 e^{j\varphi_1} z_3 e^{j\varphi_3} = z_2 e^{j\varphi_2} \cdot z_4 \cdot e^{j\varphi_4}, \qquad (1)$$

where z_1, z_2, z_3, and z_4 are the moduli of the total resistance of the bridge arms; $\varphi_1, \varphi_2, \varphi_3, \varphi_4$ are the voltage phases on these arms; [footnote cont.]

diode D_2 in the other branch of the bridge. Thus the zero reading of the galvanometer at balance is achieved without any of the complications connected with comparison of two constant voltages, as occurs in the usual four-arm dc bridge.

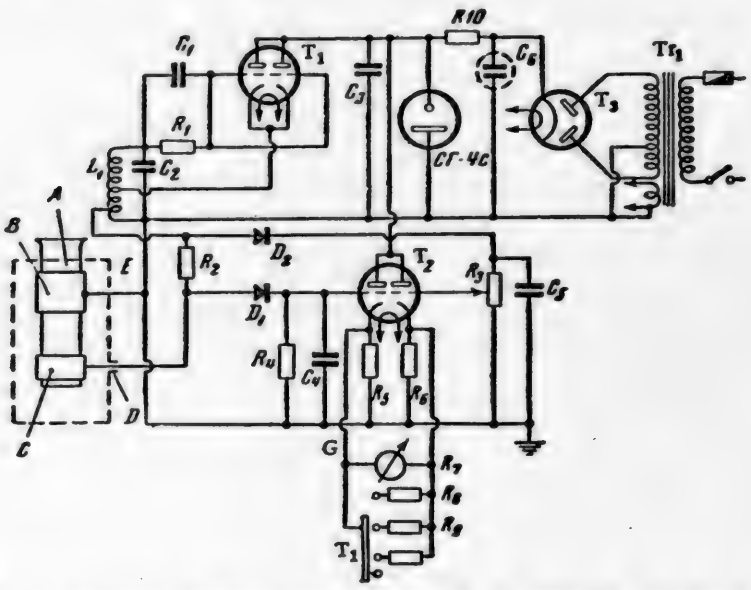

Fig. 2. Schematic diagram of the apparatus: T_1, T_2) 6N1P; T_3) 5TsChS; D_1, D_2) DG–Ts6; Tr) transformer; (ELS-2); A) cell (in a screen); G) μA-microammeter type M-24.

It should be pointed out that the principle of an ac bridge, but with a constant displacement of the voltage from the rectifier in the measuring diagonal, has been known for some time [4, 5] but has not been used in the field of high-frequency titration [6-8].

2. Principal Scheme of the Apparatus (Fig. 2). The high-frequency generator (35 megacycle was assembled on the basis of a 6N1P tube on the usual three-point scheme, the generator being supplied from a stabilized rectifier. The generator supplies two circuits simultaneously; one of these circuits consists of the additional resistance R_2 and the cell A. The voltage applied to the cell is rectified by the diode DG-Ts6. The voltage rectified by this diode proceeds from the load R_4 (with a blocked condenser C_4) to the grid of the first triode Li(6N1P). The other, the compensation circuit, fed by the generator, consists of a germanium diode D_2 (DGTs6), and a load R_3 with a blocked condenser C_5. Under these conditions, the compensating voltage

••[Footnote continued from previous page] From (1) it follows that:

$$z_1 \cdot z_3 = z_2 \cdot z_4$$
$$\varphi_1 + \varphi_3 = \varphi_2 + \varphi_4 \qquad (2)$$

Equation (2) is a condition for the balance of an ac bridge; it should be balanced with respect to the moduli of resistance and voltage. To achieve this it would be necessary to introduce not less than two regulated parameters – active and capacitive resistance.

applied to the grid of the second arm of the triode T_1 can be regulated so as to obtain a null reading of the indicator galvanometer G.•

The galvanometer G is connected between equal cathode resistances R_5 and R_6, and is shunted by one of the resistances R_7–R_9 for obtaining various limits for the measurements; by altering the shunt, it is possible to use 100, 80, 60, 40, and 20% of the maximum sensitivity of the apparatus; this permits titration to be carried out over a wide concentration range for the test solutions (10^{-3} N – 5 x 10^{-1} N with respect to HCl).

The oscillating circuit L_1C_1 of the generator is calculated so that the frequency of the oscillations generated is equal to 35-40 megacycles. This frequency, in conjunction with the types of cells we used, permit work to be carried out with solutions with a high concentration (e.g. in the case of HCl, up to 5 x 10^{-1} N), since the capacitive resistance $X_{ct} = \frac{1}{w} C_{ct}$ between the lining and the solution is sufficiently small in this case [1].••

In order to line up the output resistance of the generator with the resistance of the cell circuit (i.e. in order to make more efficient use of the power supplied by the generator) the voltage in the cell circuit is taken from some of the windings of the induction coil L_1 of the oscillating circuit L_1C_2. The grid-leak C_1R_1 is included for the purpose of increasing the stability of the operation of the generator and its efficiency.

3. Construction of the Apparatus. The general appearance of the apparatus is shown in Fig. 3; its dimensiions are 215 x 105 x 214 mm. The transformer Tr (LS-2), the 5Ts4S tubes, SG-4S, the high-frequency generator (based on the tube 6N1P), the amplifier (based on tube 6N1P), and the other elements of the setup are mounted on the chassis of the apparatus. Two sockets are included in the left hand side of the chassis for connection with the cell block. The lower socket is a high-frequency "staker" connected with generator, while the upper socket is a metallic insert embedded directly in the wall of the housing ("ground connection").

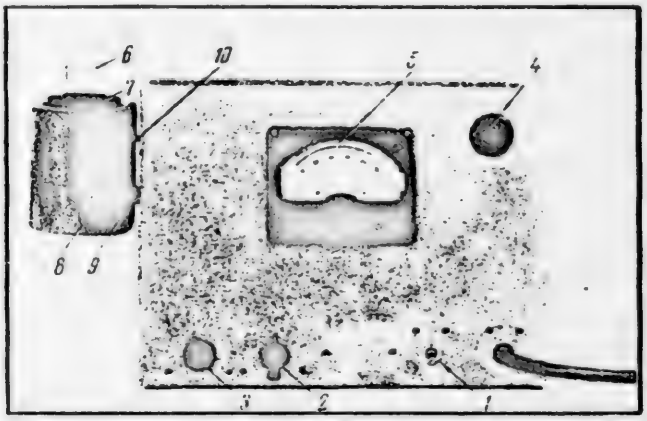

Fig. 3. General appearance of the apparatus.

The cell block consists of a thin-walled test tube 6 with two metallic bands wrapped round its outer walls (around its circumference). The test tube is mounted by means of rubber ring 7 in a metal screen 8 which has two brackets on its side wall; the lower one 9 is insulated from the body of the screen and is connected with the lower band on the test tube; the upper one 10 is embedded in the screen wall ("ground connection"), and is connected with the upper band on the test tube. By means of these two brackets, the cell in the screen is tightly packed into the appropriate socket on the side wall of the apparatus.

•In the apparatus described earlier for high-frequency titration, compensation of the initial voltage was realized by galvanic elements [1, 2, 9]; as a result of this the readings of the apparatus depended to a very large extent on the grid voltage, since when the latter was used, the voltage across the cell changed while the compensating voltage remained constant. This limited the sensitivity of the apparatus and did not allow the use of an amplifier.

••Titration of concentrated solutions (of the order of 0.5–1 N) has been achieved by other authors by resorting to the use of the beat method [10] involving the use of a generator operating at a few hundred megacycles. This complicates the apparatus considerably.

A tumbler switch 1 is fitted onthe face panel of the apparatus for switching on the supply (from the network); onto this panel are also fitted the handle 3 of the potentiometer for adjusting the zero, the arm 2 of the throw-over switch for the shunting resistances, the signal lamp 4 and the microammeter for measuring the constant high-frequency current passing through the cell.

The apparatus is used as follows. After the cell with test solution has been inserted in position, the apparatus is switched on for 20 minutes before the start of a titration. Using 2, the optimum sensitivity for the given concentration is set. The microammeter needle is set to the beginning or end of the scale by means of 3, depending on the direction taken by the changes in the current during titration. The equivalence point is established graphically – by the intersection of the left and right branches of the titration curve [1].

4. Application. The apparatus assembled on the basis of the scheme outlined above can be used for solving various analytical problems which turn up in factory and research work. Express methods – which are at the same time fairly accurate–have been developed for the quantitative determination of phenols, cresols, inorganic and organic acids and bases in dark-colored solutions containing suspensions and emulsions of synthetic resins; methods have been suggested for the determination of the total acidity of mineral oils, and for the determination of acetic acid in mixtures with sulfuric acid, and in mixtures with acetic anhydride [11, 15].

Of considerable interest is a method for the determination of ammonia in aqueous suspensions of latex used in the rubber industry.• A known volume of the latex suspension is placed in the cell for high-frequency titration, and titrated with HCl with constant agitation. The first break on the titration curve corresponds to neutralization of ammonia (Fig. 4). The latex begins to coagulate at this point. The second break on the

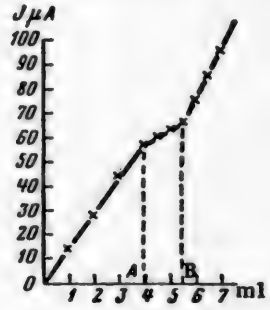

Fig. 4. Titration of ammonia in an aqueous suspension of latex with HCl: A) Neutralization point of ammonia; B) point corresponding to completion of coagulation of the latex.

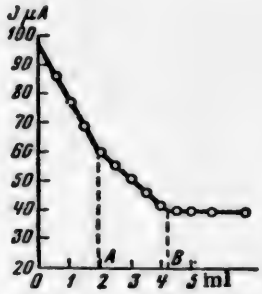

Fig. 5. Back titration of o-nitraniline in glacial acetic acid. To 10 ml of a solution of o-nitraniline was added excess (2.5 ml) 0.3865 N $HClO_4$. Titration was carried out with 0.2126 N CH_3COONa solution: A) Amount of sodium acetate used to titrate excess acid; B) amount of sodium acetate used to titrate o-nitraniline.

titration curve corresponds to completion of coagulation; at this point, the deposited latex sticks to the stirrer used for agitating the mixture. By means of this apparatus it is possible to carry out high-frequency titration in nonaqueous media, under conditions where a choice has been made of the most suitable solvent for the given purpose [12, 13].

In Fig. 5 is shown the back-titration curve of o-nitraniline.•• In this method, an excess of standard perchloric acid is added to a known volume of test solution in glacial acetic acid; high-frequency titration is then carried out in perchloric acid, using an acetic acid (anhydrous) solution of sodium acetate of known strength as titrant. This first break on the titration curve corresponds to excess $HClO_4$, while the second break corresponds to the content of o-nitraniline.

• This work has been carried out by one of the authors in conjunction with V. N. Provorov and S. A. Nikitina (Institute of the Rubber Industry of the USSR Ministry of Chemical Industry).

•• According to the results of A. A. Nemodruk and V. A. Frolkina.

According to preliminary results, by using the apparatus described in conjunction with a differential solvent [14] (acetone + water), it is possible to determine the equivalence point during titration of weak organic acids (or their total) of the type of ortho-, para-, or meta- chlorophenols by an aqueous acetone solution of NaOH.•

SUMMARY

A highly-sensitive, portable instrument has been developed for high-frequency titration; this apparatus is easy to construct and operate. By means of this apparatus it is possible to carry out titration over a wide concentration range (0.5 N – 1×10^{-3} N); it can also be used for studying various reactions in nonaqueous media.

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Received October 2, 1957

•According to the results of K. Kh. Arkhipova and R. F. Iliukhina.

••Original Russian pagination. See C.B. Translation.

•••In Russian.

••••Russian translation.

A PHOTOGRAPHIC METHOD FOR MEASURING THE INTENSITY OF THE COLOR OF SOLUTIONS IN SMALL VOLUMES

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For the determination of very small amounts of materials, microspectrophotometry can be successfully used in addition to ultramicrochemical methods [1,2], since in the case of small volumes of solution, the amount of material necessary for analysis is very little (when one takes into account the sensitivity of the photometric method which allows one to operate with very dilute solutions).

There are published descriptions of a few types of cells which, in combination with photometers (in particular, the photoelectric spectrophotometer SF-4), can be used for measuring the intensity of the color of small volumes of solution [3, 4].

In the present article, which is devoted to work carried out in 1949, a description is given of a simple apparatus for a photographic method of measuring the intensity of colors of solutions in capillary cells which have a capacity of 0.05-0.1 ml.

The Principles of Operation of the Apparatus. The apparatus is shown schematically in Fig. 1. The test solution is poured into cell 1, while the other cell 2 is filled with solvent or a standard solution whose concentration should be less than the concentration of the test solution. Both cells are placed alongside each other in the path of a beam of light, directly in front of the photographic plate 3 arranged perpendicularly to the axis of the cell. After the photographic plate has been fixed in position it is possible to detect on it the images of the openings of both cells. For a given exposure, the intensity of blackening of the plate will depend on the brightness of the pencil of light passing through the cell; the blackening will be less, the higher the concentration of the solution. A continuous optical reducer (attenuator) 4 is placed in front of the reference cell 2;

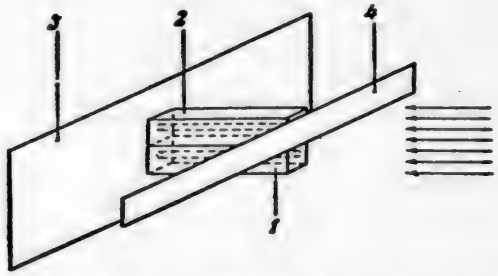
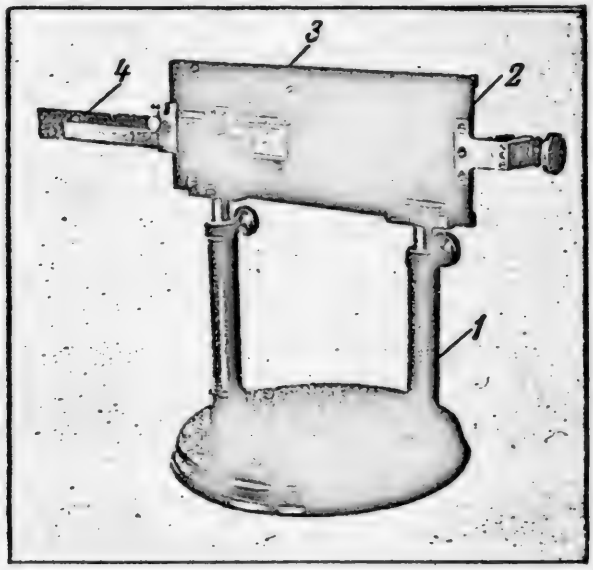


Fig. 1. Schematic diagram of the microcolorimeter. 1) Cell containing test solution; 2) cell containing standard solution; 3) photographic plate; 4) optical reducer (attenuator).

by shifting this reducer it is possible to find a position corresponding to equal blackening of both images. In such a case, it can be assumed that the absorption of the test solution is equal to the total absorption of the

light by the standard solution (or solvent) and the corresponding part of the reducer. Using a series of solutions with known concentrations, a calibration curve is constructed for the given standard solution within the coordinates: concentration of solution – position of the reducer, denoting the place of equal blackening. Having filled the cell with test solution, and having established the position of the reducer at which equal blackening



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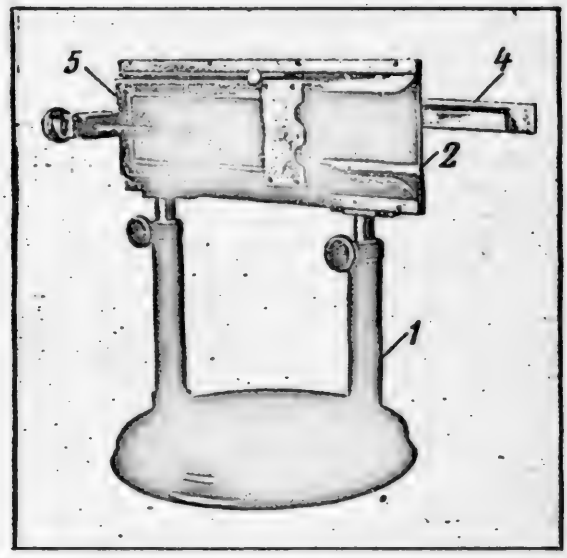

b

Fig. 2. General appearance of the microcolorimeter. a) Appearance from the front; b) from the back; 2) plate; 3) tube with shutter; 4) frame with attenuator; 5) cassette with photographic plate.

is obtained, the concentration of the test solution is then determined by means of the calibration curve. When the percentage reduction is known for each part of the reducer, then the concentration of the test solution can

be calculated directly on the basis of Beer's law without resorting to the calibration curve.

Construction of the Apparatus. The general appearance of the apparatus is shown in Fig. 2. The apparatus consists of two parts – a lower, massive base 1 and the upper plate 2 fitted on it. On the front of the plate is located a tube 3 with a shutter in which there is a rectangular opening for the cell, and also a groove along which the frame, to which the optical attenuator 4 is fastened, moves. The attenuator is fixed so that it only darkens the upper cell; its position is fixed by means of a scale with a vernier.

On the back side of the plate there are longitudinal grooves along which, by means of a screw, the cassette 5 with the photographic plate (4.5 × 12 cm) is moved. For establishing the position of the cassette on the plate, a special scale is inscribed (as in an ordinary spectrograph).

Cell. The cell is illustrated in Fig. 3. It is made as follows. By means of a milling machine a groove about 1 mm deep is cut in the middle of a stainless steel plate (5 × 10 × 50 mm), the edges of the groove being made strictly parallel to the edges of the plate. Two small blocks, also of stainless steel and measuring (5 × × 5 × 10 mm) are screwed into the steel plate at each end of the groove; they are screwed in along one of the 5 mm edges (see diagram). The ends of the plate and the corresponding surfaces of the blocks are ground parallel to one another and are polished. The shape of the openings at both ends of the cell should be exactly the same. Brass rings (diameter 10/7 mm, length 10 mm) are screwed into the end faces (or soldered with tin). A glass plate (10 × 40 mm) which covers the groove is accurately stuck onto the inner side of the cell by means of grease (e.g. picene). Before proceeding to fill the cell with solution, the opening at one of the ends is closed by means of a polished, plane, parallel, round window. For this purpose, the glass window is pressed onto the end surface by means of a small washer (diameter 7/3 mm, length 3 mm) with a slit for opening, screwed into the brass ring.

The cell can be filled in two ways depending on whether a large or small amount of solution is available. When the amount of solution is considerably in excess of 0.05 cm^3 (standard solutions, solvent, etc), a glass tube can be used, having a diameter of 4-5 mm, whose end has been drawn out 70-80 mm to give an evenly cut opening with a diameter of 0.5-0.7 mm. Having taken up the solution in such a pipet and holding the cell in a horizontal position, the drawn out end is introduced into the cell so that it touches the bottom of the latter. By gradually inclining the cell, the solution is allowed to fill the cell slowly, taking care to see that no bubbles of air remain. During the filling process the pipet is gradually withdrawn from the cell, ensuring that the tip of the pipet is always immersed to a depth of 2-3 mm in the solution. When the cell has been filled, and the liquid meniscus is convex on the open side of the cell, the cell is sealed with the glass window, and the latter pressed home with the washer as indicated above. If there should be observed any bubbles of air, however small, on the walls of the cell, then the latter is shaken so that the bubbles accumulate at one of the ends, the window is then withdrawn, and a small amount of liquid added until a convex meniscus is formed; the end is finally sealed.

When the amount of liquid available is very small, then the cell should be filled under the microscope (× 25 – 30), using for this purpose a micropipet fitted with a piston attachment instead of the pipet described above; the construction of such a micropipet has been worked out and described by us previously [5]. The cell is fixed on a plate connected with the microscope stage so that the canal of the cell is in the field of vision; then by screwing the piston setup of the micropipet, the cell is filled as described above. The solution can be taken out of the cell by the same method.

Filling and emptying the cells are most important operations. It is essential that the glass windows be accurately and tightly fitted. If optical contact is not achieved then the solution will gradually evaporate, and bubbles of air may appear in the cell. For better hermetical sealing in such cases, the edges of the windows are smeared with a thin film of thick grease; care is taken during this operation that the grease is uniformly distributed in the form of a circle around the periphery of the windows, and that it does not extend beyond the openings of the cells. In order to avoid liberation of bubbles of dissolved air, it is recommended that the test solutions, etc. be heated to 40-50° before filling the cell.

A compensating setup may be used for obtaining a parallel beam of light, or the source of light may be set up at a long distance from the apparatus. We used the second variant. A 500 watt heating lamp set up at a distance of 5 meters from the apparatus was used as the light source.

The apparatus can be shifted and rotated during focussing; it is fairly stable, and the small forces associated with moving the cassette and the attenuator, and also with opening and closing the shutter do not affect its position. During focussing, the upper plate with the tube and cassette can be moved in a vertical position and can be fixed by means of screws.

Optical Attenuator. The continuous optical attenuator is a glass plate (15 x 180 mm), the blackening of which gradually increases on going from one end to the other of the plate. The preparation of a continuous attenuator by vacuum deposition of metal (usually plate metal) is in itself a fairly complicated problem. An attenuator can, however, be prepared in any laboratory from a piece of photographic plate as follows. An exposed, developed, and fixed photographic plate is placed in a vessel which is filled at a definite rate with a bleaching solution. By altering the rate at which the bleaching solution is poured in, it is possible to prepare an attenuator in which the blackening changes continuously. After bleaching the plate is fixed, washed, and dried. An attenuator could also be prepared by using a developer instead of a bleach, and treating the exposed photographic plate soaked in water. One should bear in mind that there is no linear relation between the bleaching time (and even more so, the developing time) and the blackening intensity, so that even for regular movement of liquid along the plate, the attenuators thus prepared are not linear. Moreover, the attenuators prepared in this way are not strictly grey. This, however, does not prevent them from being used in the method described. One of the cells is filled with standard solution, while the other is filled with test solution. Both cells are fitted together as shown in Fig. 3b (the position of one cell relative to the other is fixed by pins) and are placed in the rectangular opening of tube 3 of the apparatus (Fig. 2).

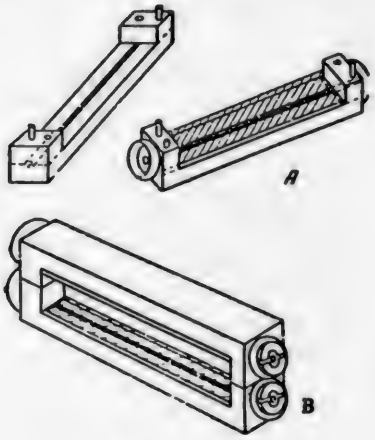

Fig. 3. Cell.

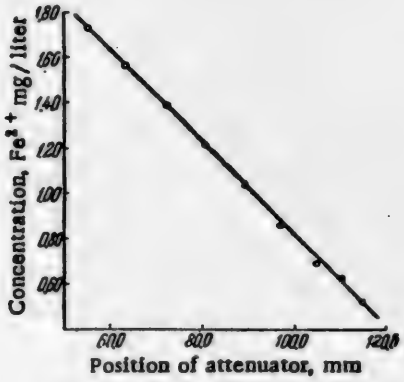

Fig. 4. Calibration curve.

Method of Measurement. The apparatus is set up in such a way that the cells are arranged on the level of the light source, while only one image of the incandescent filament can be seen through the opening. The correctness of the focussing is checked by means of a piece of frosted glass, the image of the opening on which should be sharp both for a small distance of the glass from the cell, and when this distance is increased to 5 - - 10 cm. By regulating the brightness of the lamp, the exposure at which normal blackening is obtained is established. The cassette plus photographic plate is placed in the apparatus and the shutter closed, after which 50 pairs of spots are photographed on the plate (at 2 mm intervals), while the attenuator and the cassette plus plate are moved. After development a pair of spots with equal blackening are sought for on the plate (visually, or by means of a microphotometer).

In order to establish more accurately the position of the attenuator corresponding to uniform blackening, the process of taking photographs may be repeated, the attenuator in this case being moved through shorter distances. The concentration of the solution is established by means of the calibration curve.

In order to increase the sensitivity of the method described, it is possible to use a light filter, the transmission region of which corresponds to the maximum absorption of light by the test solution. Naturally, when this is done, the concentration range which the given attenuator covers will be restricted. In those cases where

it is desirable to extend the concentration range at the expense of the accuracy of the method, one can place a light filter which passes light in the region of weak absorption of the solution, in front of the cells. The conditions of work with white light is the mean of the two cases indicated. When a light filter is used, it should be borne in mind that the same one should be used both for constructing the calibration curve and for making measurements on the test solution.

The spectral sensitivity of the emulsion of a photographic plate has the same effect as the spectral characteristics of light filters; when the region of maximum sensitivity of the emulsion corresponds to the region of strong absorption of the solution, then the sensitivity will be increased, but the region of concentration covered by a given attenuator will decrease, and vice-versa. Accordingly, all measurements on the test solution should be carried out on photographic plates with the same kind of emulsion as that used for constructing the calibration curve (reproducing).

In Fig. 4 is shown, as an example, a calibration curve which we constructed for the quantitative determination of iron in the form of the colored complex of Fe^{2+} with o-phenanthroline. The concentration of iron in the test solutions varied over the limits $0.5 - 2 \times 10^{-3}$ g/liter. Accordingly, the amount of iron in the test solution (0.1 ml) amounted to $0.5 - 2 \times 10^{-7}$ g. Differences in the positions of the attenuator during replicate measurements carried out on the same solution, or on independently prepared solutions of the same concentration, did not exceed 0.5 mm; this corresponded to an error of $\pm 1 \times 20^{-9}$g Fe.

SUMMARY

A simple apparatus is described for the photographic measurement of the color intensity of solutions, in which a cell with a capacity of 0.05 – 0.1 ml is used.

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Received June 21, 1956

*Russian translation.

**Original Russian pagination. See C.B. Translation.

COPRECIPITATION OF CESIUM WITH SPARINGLY SOLUBLE DIPICRYLAMINES

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Dipicrylamine (hexanitrodiphenylamine) was first suggested by Poluetkov in 1933 [1] as a sensitive reagent for potassium. Since that time the soluble sodium and magnesium salts of dipicrylamine have found fairly wide application both for the qualitative detection of potassium, rubidium, and cesium, and for the quantitative determination of these elements [2-6].

Despite the fact that quantitative determinations of the alkali metals indicated, by means of dipicrylamine are carried out fairly often the possible coprecipitation of ions with precipitates of the dipicrylamine salts has not yet been studied. We were unable to find any published references to the coprecipitation of cesium with the sparingly soluble dipicrylamines of potassium, rubidium, thallium, and ammonium.

Meanwhile, taking into account their chemical similarity, the fact that their valencies are the same, and that the ionic radii of cesium, potassium, and thallium are similar to each other, one might expect that cesium would be coprecipitated with the dipicrylamines of these elements.

We studied the coprecipitation of cesium with the dipicrylamines, using the radioactive isotope Cs^{134} as an indicator. The initial specific activity of the preparation amounted to 130-170 impulses/minute per γ of cesium. The precipitant used was a 1% solution of sodium dipicrylamine.

Precipitation was carried out as follows. Into a series of centrifuge tubes were introduced 1-ml lots of solution containing 1 mg of potassium or 2.5 mg of thallium, as well as 12 γ of cesium; precipitation was effected by addition of 1-3 ml of sodium dipicrylamine. After one hour, the tubes were centrifuged and the cesium content of the mother liquors determined radiometrically. The mother liquors were then removed, and the precipitates transferred to filters, which were first washed with ether and then with iced water, and finally dried to constant weight.

In order to exclude the effect of the appreciable solubility of the precipitate, we determined not only the absolute amount of coprecipitated cesium, but also the amount of it in 1 mg of the precipitate.

Preliminary tests showed that cesium is almost completely coprecipitated with the dipicrylamines of potassium, rubidium, and thallium.

In order to make effective use of the coprecipitation of cesium for the purposes of concentrating the latter, we studied the nature of this process.

First of all we investigated the effect of temperature on the coprecipitation of cesium with potassium and thallium dipicrylamines. For this purpose, the working solutions were thermostated at various temperatures prior to mixing (Table 1).

As the results given in Table 1 show, on increasing the temperature from 0 to 30°, coprecipitation of cesium with potassium dipicrylamine remains almost complete. On increasing the temperature further, the amount of cesium coprecipitated decreases as the result of the increasing solubility of the precipitate but the cesium content per unit weight of the precipitate of potassium (or thallium) dipicrylamine remains constant at the

TABLE 1

Coprecipitation of Cesium with Potassium and Thallium Dipicrylamines as a Function of Temperature (12 γ cesium, 1 mg potassium, or 2.5 mg thallium)

Macro-component	Temp.	Cs coprecipitated in γ	Cs coprecipitated in %	Wt. of prec.	Cs, in γ/mg prec.
Potassium	0	11.7	97	9.3	1.3
	15	11.7	97	9.3	1.3
	30	11.4	95	7.9	1.4
	40	10.0	83	7.2	1.4
	80*	—	—	—	—
Thallium	0	11.8	98	9.0	1.3
	15	11.8	98	8.4	1.4
	30	11.7	97	9.0	1.3
	40	11.9	99	8.5	1.4
	80	11.7	97	8.0	1.5

*At this temperature the residue of potassium dipicrylamine dissolves completely.

various temperatures. This signifies that temperature changes have no effect on the coprecipitation of cesium with the dipicrylamines.

We next studied the adsorption of cesium on aged precipitates of potassium and thallium dipicrylamines, prepared from 1 mg potassium or 2.5 mg thallium (Table 2).

Were the coprecipitation of cesium mainly the result of adsorption processes, then one might expect that as in the previous experiments, there would be almost complete transfer of cesium from solution to precipitate. Accordingly, on aging the precipitate for 48 hours, there should be a considerable decrease in coprecipitation. This however was not observed; this fact, coupled with the results shown in Table 1 and 2, testify to the isomorphous character of the coprecipitation of cesium with potassium and thallium dipicrylamines.

The results given in Table 3 show that the third component does not affect coprecipitation of cesium; the extent of adsorption coprecipitation also depends on the order in which the reagents are added to each other. We investigated the influence of this factor on coprecipitation of cesium. It was found that the order in which the solutions are added has no effect on the amount of coprecipitated cesium. Cesium, here again, is almost completely coprecipitated with potassium and thallium dipicrylamines.

TABLE 2

Adsorption of Cesium on Aged Precipitates of Potassium and Thallium Dipicrylamines (12 γ cesium)

Precipitate	Cesium adsorbed in γ	Cesium adsorbed in %
Freshly prepared potassium dipicrylamine	2.5	21
Potassium dipicrylamine allowed to stand for 48 hours	2.6	22
Freshly prepared thallium dipicrylamine	1.3	11
Thallium dipicrylamine allowed to stand for 48 hours	0.8	7

From Fig. 1 it is evident that with increasing amounts of the macro-components (thallium and potassium), or decreasing amounts of the micro-component, the amount of cesium in 1 mg of precipitate always decreases. Consequently, the amount of coprecipitated cesium in the precipitate depends, not so much on its absolute amount, but on the proportions of cesium and potassium, and also of cesium and thallium in the solution prior to precipitation.

Cesium is almost completely coprecipitated with the precipitates of potassium and thallium dipicrylamines in all cases.

Thus, variations in the conditions used for carrying out the tests have no effect on the coprecipitation of cesium with the dipicrylamines. We accordingly again came to the conclusion that this coprecipitation is isomorphous in character.

TABLE 3

Coprecipitation of Cesium (12 γ) in the Presence of a Third Component

Macro-component	Macro-component content mg/ml	Third component	Cs coprecipitated in γ	Cs coprecipitated in %	Wt. of prec.	Cs, γ / mg prec.
Potassium	1.0	None	11.5	95	10.4	1.1
	1.0	Rubidium	11.0	91	10.0	1.1
	1.0	Thallium	11.0	91	9.9	1.1
	1.0	Magnesium	12.0	100	10.7	1.1
Thallium	2.5	None	11.4	95	7.2	1.8
	2.5	Rubidium	11.6	96	6.5	1.8
	2.5	Thallium	11.5	95	6.2	1.9
	2.5	Magnesium	11.7	97	7.0	1.7

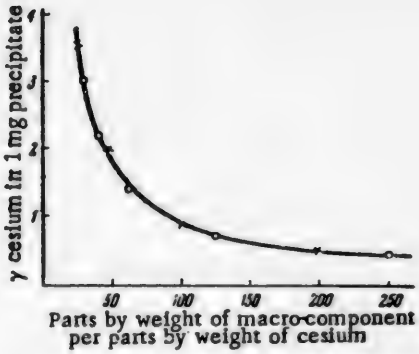

Fig. 1. Coprecipitation of cesium as a function of changes in the amounts of the macro- and micro-components. x) Experiments carried out with a constant amount of cesium; o) Experiments carried out with a constant amount of potassium or thallium.

In order to study the effect of the amount of precipitant on the coprecipitation of cesium with potassium dipicrylamine, we carried out experiments on the precipitation of the same amount of potassium (1.0 mg):

a) with the stoichiometric amount of sodium dipicrylamine;

b) with an amount of sodium dipicrylamine twice the stoichiometric amount;

c) with amounts of sodium dipicrylamine one half and one quarter the stoichiometric amounts.

About 12 mg of sodium dipicrylamine is the theoretical amount required for precipitation of 1 mg of potassium.

The experimental results (Table 4) show that with decreasing amount of precipitant the amount of coprecipitated cesium decreases, but the amount of coprecipitated cesium increases per unit weight of the precipitate as the weight of the latter decreases. This can be explained by the fact that the Khlopin constant in this case is greater than unity. Similar experiments were carried out with rubidium, thallium, and ammonium dipicrylamines (Tables 5-7).

The results given in Tables 4-7 are illustrated graphically in Fig. 2. The amount of the precipitated macro-component calculated as a percentage, from the weight of precipitate obtained, is plotted along the abscissa. We see that, other conditions being equal, most cesium is coprecipitated with ammonium dipicrylamine. The hypothesis can be advanced that the Khlopin constant is of greater importance during the coprecipitation of cesium with ammonium dipicrylamine, and of lesser importance with the corresponding salts of potassium and thallium, while in the case of rubidium dipicrylamine, Khlopin's constant approximates to unity. We did not calculate this constant, since, for the comparatively short time interval necessary for carrying out separate tests, the system only approximates to a thermodynamic equilibrium between the amount of cesium and the macro-component in the solution and precipitate.

The almost complete coprecipitation of cesium with the dipicrylamine precipitates enables one to develop a method for its concentration. Precipitation of 10 mg of the macro-component (potassium, thallium) and 12 γ of cesium contained in 100 ml of solution, was effected by addition of 200 mg of sodium dipicrylamine. The cesium content of the precipitate separated from the mother liquor after standing for 24 hours was

TABLE 4

Coprecipitation of Cesium with Potassium Dipicrylamine as a Function of the Amount of Precipitant for a Constant Amount of Potassium (1 mg potassium and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	K prec., %	Cs, γ/mg prec.
	in γ	in %			
2	11.7	97	10.7	88	1.1
1	11.4	95	10.4	85	1.1
0.5	9.9	83	5.1	42	2.2
0.25	6.5	54	2.3	20	2.3

TABLE 5

Coprecipitation of Cesium with Rubidium Dipicrylamine as a Function of the Amount of Precipitant (2.5 mg thallium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Rb prec., %	Cs, γ/mg prec.
	in γ	in %			
1	11.3	94	14.0	91	0.8
0.5	5.0	42	7.5	49	0.7
0.25	2.6	24	3.0	19.5	0.8
0.125	1.6	13	2.5	16.2	0.7

measured radiometrically. It was found that under these conditions about 75% of the cesium was concentrated in the precipitate. By carrying out a threefold precipitation it is possible to concentrate practically all the cesium found in the original solution.

On decreasing the amount of cesium in 100 ml of solution to 0.01 γ (specific activity, 70,000 impulses/minute per γ of cesium), about 85% of the cesium is concentrated in the precipitate.

TABLE 6

Coprecipitation of Cesium with Thallium Dipicrylamine as a Function of the Amount of Precipitant (2.5 mg thallium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Tl prec., %	Cs, γ/mg prec.
	in γ	in %			
2	11.4	94	4.7	60	2.4
1	11.5	95	5.0	63	2.3
0.5	6.5	55	3.0	38	2.2

TABLE 7

Coprecipitation of Cesium with Ammonium Dipicrylamine as a Function of the Amount of Precipitant (1 mg ammonium, and 12 γ cesium)

Moles precipitant per mole K	Cs coprecipitated		Wt. of prec., mg	Ammonium prec., %	Cs, γ/mg prec.
	in γ	in %			
1.5	11.9	99	9.1	36	1.3
1	11.8	98	6.3	25	1.9
0.5	11.9	99	4.0	16	2.9

It is best to carry out separation of traces of cesium by means of ammonium dipicrylamine, which is readily broken down and removed. 100 ml of solution containing 70 mg of ammonium nitrate and 12 γ cesium

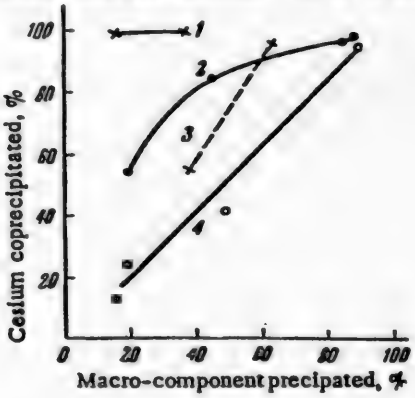

Fig. 2. Coprecipitation of cesium as a function of the amount of coprecipitated macro-component: 1) precipitation of ammonium dipicrylamine; 2) precipitation of potassium dipicrylamine; 3) precipitation of thallium dipicrylamine; 4) precipitation of rubidium dipicrylamine.

was precipitated with a solution of sodium dipicrylamine. After 24 hours the precipitate was removed from the mother liquor, transferred to a crucible and heated to 300°. Under these conditions the ammonia volatilized, the dipicrylamine decomposed, and the cesium formed the oxide. The traces of oxide thus obtained were dissolved in a drop of water. In this solution cesium was detected by formation of characteristic crystals of $Cs[BiI_4]$.

In this way, sparingly soluble dipicrylamines, particularly ammonium dipicrylamine, can be used as carriers for isolating traces of cesium from very dilute solutions.

SUMMARY

It has been established that cesium can be isomorphously coprecipitated with the sparingly soluble dipicrylamines of the alkali metals and thallium. It has been shown that thallium and ammonium dipicrylamines can be used as carriers for removing traces of cesium from very dilute solutions.

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Received May 11, 1956

SPECTROGRAPHIC DETERMINATION OF CALCIUM, MAGNESIUM, ALUMINUM, SILICON, AND TIN IN REFINED RHODIUM AND IRIDIUM

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During the analysis of noble metals it is often necessary to determine calcium, magnesium, aluminum, silicon, and sometimes tin which are present in small amounts difficult to evaluate by normal chemical methods. Determination of the metals indicated as impurities in refined metals should be possible by means of spectrographic analysis. During the analysis of rhodium and iridium for these elements, the metal was brought into solution and the latter evaporated in an ac arc. The success of the analysis was found to depend to a considerable extent on the use of accurately prepared standards. During the development of a technique for analyzing rhodium for its content of the elements indicated above, the starting material for preparing standards was a very pure preparation of rhodium trichlorotriamine. Nevertheless, even this preparation contained calcium, which, despite careful and repeated precipitation of the trichlorotriamine, still showed up on the spectrograms. This small amount of calcium, which possibly came from dust in the air, was taken into account in our calculations, by extrapolation. The reprecipitated rhodium trichlorotriamine was decomposed by heating in a crucible oven and was reduced in a hydrogen stream. The rhodium metal was dissolved by the aid of chlorination [1].

A few grams (3-4) of the metallic rhodium was carefully ground in an agate mortar to a very fine powder. The powder was strewn into a quartz, round-bottom flask sealed with a ground glass stopper with two outlet tubes for gas. The flask was placed in a crucible oven which could be heated to 800-900°. When the temperature in the oven had reached 200°, chlorine was passed from a cylinder into the flask, the chlorine having been washed beforehand with water in a wash bottle. Chlorine was passed through the apparatus for an hour at the rate of 2-3 bubbles per second. In the course of this time, the temperature was gradually taken up to 700°. Heating was discontinued at the end of the hour, the flask removed from the oven and cooled in air; its contents — rhodium chloride — was transferred to an agate mortar, to which was then added sodium chloride equal to twice the amount of the rhodium chloride, and the whole thoroughly ground up and mixed. The ground mixture was then replaced in the original quartz flask. The flask was placed in the crucible oven, and chlorine passed through again at the same rate as before. The temperature was raised to 700-800° and kept at that temperature for 20-25 minutes. The whole chlorination process took about an hour. At the end of this period the oven was switched off and the flask left in the oven until the latter had cooled completely, otherwise the flask might have cracked because of the rapid crystallization of the fused salts.

The contents of the cooled flask were dissolved in 90 ml of twice-distilled water. The insoluble residue was filtered off. The volume of the solution was made up to 100 ml. 5 ml of this solution was taken and its rhodium content determined chemically. This solution of sodium chlororhodiate plus some sodium chloride was taken as the stock solution for preparing the standard solutions.

The impurities to be determined were taken in the form of solutions of the following salts: calcium sulfate, the double sulfate of magnesium and aluminum, aluminum nitrate, sodium silicate, and tin chloride. Sodium silicate was prepared by fusing chemically pure silica with sodium carbonate, the melt formed being dissolved in water and the silicon content determined chemically.

Using these solutions of sodium chlororhodiate and the salts of calcium, aluminum, silicon, and tin, standard solutions were prepared by mixing; the standard solutions prepared contained the impurities to be determined in amounts aranging from 0.065 to 0.0003% with respect to rhodium. The rhodium concentration was 0.5%.

The standard solutions prepared in this way were placed in a discharge tube with carbon electrodes. The gap between the carbon electrodes was kept at 3 mm.

An ac arc was used for excitation.

The current used had a value of 3 amperes. The exposure time for calcium and magnesium was 3 minutes, while for silicon, aluminum, and tin at low concentrations, it was 5 minutes. Solution was added to the discharge tube every 1.5 minutes during the exposure. Each standard solution was exposed three times.

The electrodes were arced for 10-15 minutes prior to each exposure. The spectra were photographed on NIKFI spectrographic plates type II. The plates were developed in a metol-hydroquinone developer. Photometric measurements were carried out with a Zeiss microphotometer.

Determination of Calcium. The following pairs of lines were chosen for the spectrographic determination of calcium:

Ca I 4226.728 A – Rh I 4196.504 A
Ca II 3968.468 A – Rh II 3975.314 A

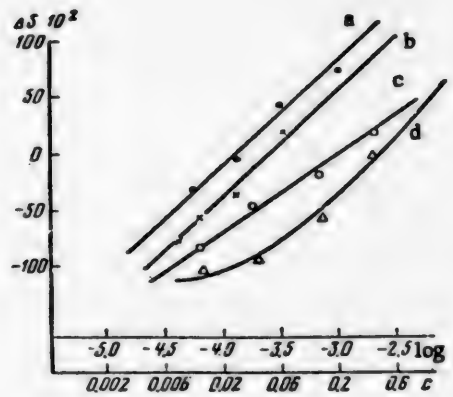

Fig. 1

The calibration curves for each pair of lines (Fig. 1 a, b) covered the concentration range of calcium in rhodium from 0.06 to 0.002%. Both pairs of lines gave steep curves with a slope for the first pair of 44° (tan α = = 0.966), while for the second the slope was 49° (tan α = = 1.150).

The amount of calcium in the original rhodium was determined graphically; i.e. the spectrum of the solution of pure rhodium was also photographed; the results of the photometric measurements were superimposed on the curve and the calcium content found by extrapolation. On the basis of the calcium content found, corrections were applied to its concentration in the standard solutions.

The spectra of the solutions were photographed on several plates. On plates of the same type, the tangent of the slope of the curve varied little around the values given above.

The mean arithmetical error for determination of calcium by means of the first pair of lines, on the basis of several negatives, amounted to 11% for the concentration range 0.065-0.005. For the second pair this error was 9%.

During analysis for calcium the lower concentration limit was set by the content of the element to be determined in the rhodium. If rhodium of higher purity with respect to calcium were available, the concentration of the latter which could be determined could be lowered by one order.

Determination of Magnesium in Rhodium. The standard solutions used contained 0.0035, 0.0065, 0.0235, and 0.0635% magnesium with respect to rhodium.

The following pairs of lines were chosen for analysis:

Mg I 2852.129 A – Rh I 2862.935 A
Mg I 2852.129 A – Rh II 2845.753 A

The tangent of the slope of the curve for the first pair of lines was 0.781 (angle 38°), while for the second pair of lines it was 0.869 (41°). The mean deviation for the first pair of lines on the basis of several negatives

was 7%, while for the second it was 13%; consequently, the first pair of lines are to be recommended (Fig. 2 a).

Determination of Aluminum. There was no aluminum present in the test rhodium. The pair of lines Al I 3092.713 A and Rh I 3087.415 A were chosen for photometric measurements, and also the same line for aluminum with respect to the immediate background. Since the pairs of lines Al–Rh, and Al – background both gave flat curves, errors for determination of aluminum were considerable, amounting to 20%. The curve obtained for these lines is shown in Fig. 2b.

Determination of Silicon and Tin. The calibration curve for the determination of silicon was constructed on the basis of photometric results for the following pairs of lines for silicon – rhodium:

Si I 2881.578 A – SiI – 2516.123 A
Rh 2882.366 A – RhI – 2515.746 A

(Fig. 1 c, d), for the first pair of lines the tangent of the slope was 0.649, while for the second it was 0.900.

The original rhodium contained no silicon.

The sensitivity of tin determination for contents of the latter in solution below 0.0001% was low, and the lines had low intensity; accordingly, for the determination of this element, it is necessary to have more concentrated solutions with the same ratio of tin to rhodium. Only one pair of lines were measured photometrically: Sn I 3034.121 A – Rh I 3023.911 A.

The other analytical lines of tin proved to have low sensitivity.

The deviation from the calibration curve of points corresponding to equal concentrations, as determined by the photometric results (Fig. 2 c) amounted to 17%.

In developing a method for the spectrographic analysis of refined iridium for its content of calcium, magnesium, silicon, aluminum, and tin, the first difficulty that cropped up was the absence of iridium which was spectrographically pure with respect to the impurities listed above, and the absence of a method of purifying iridium from small amounts of calcium, magnesium, and aluminum.

The iridium which we had at our disposal contained perceptible amounts of calcium and magnesium, and consequently could not serve as original material for preparing standards. It was necessary to free it from these impurities.

As in the case of rhodium, iridium was brought into solution by chlorination. An aliquot of the metal which was chlorinated with sodium chloride was almost quantitatively converted into sodium chloroiridiate.

The solution which was prepared in the same way as rhodium was spectrographically analyzed for Ca, Mg, Al, Si, and Sn. The solution of the iridium salt was found to contain calcium, so that this solution as such could not be used for preparing standards, and had to be freed from calcium.

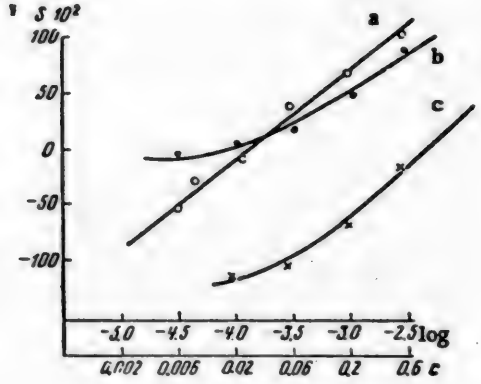

Fig. 2.

The sodium chloroiridiate obtained by chlorination was recrystallized twice, but its calcium content did not drop; accordingly, coprecipitation of calcium with lanthanum oxalate was tried.

Crystalline oxalic acid (2-3 g of acid per 3-4 g of metal) was added to the solution of sodium chloroiridiate; concentrated lanthanum nitrate was then added with stirring until the oxalic acid had been completely precipitated. The lanthanum oxalate formed should trap the calcium oxalate. The precipitate was filtered off, and some more crystalline oxalic acid added to the filtrate of sodium chloroiridiate:lanthanum nitrate was again added. This procedure was repeated three times so that all the lanthanum was precipitated.

As a result of this procedure, the calcium content of the chloroiridiate decreased appreciably. The sodium chloroiridiate purified in this way was analyzed chemically for its iridium content; for this purpose 5 ml of the solution was carefully evaporated to dryness in a tared quartz crucible on a water bath. The crucible and its contents were then calcined in a crucible oven for complete decomposition of sodium chloroiridiate. The decomposition product was carefully washed free from sodium chloride by means of hot water, and calcined in a stream of hydrogen. The reduced metal was then weighed.

From the solution of chloroiridiate whose iridium content had been determined as described above, a solution was prepared which contained 1% of iridium. The elements which were to be determined as impurities in the iridium were used in the form of the same salts as those used for the preparation of rhodium standards. The original solutions of the salts contained 0.02% each of Ca, Mg. Al, and Sn and 0.01% Si.

From these solutions, standard mixtures were prepared containing 0.5% and 3×10^{-6}% of Ca, Mg, Al, Si, and Sn taken separately; this corresponded to 0.06-0.0006% of these elements with respect to iridium.

The lower limit for the determination of calcium proved to be its content in iridium as determined by extrapolation.

Excitation conditions, conditions for taking photographs of the spectra, loading the discharge tube, etc. were similar to those used in the case of rhodium.

The following pairs of lines were chosen for determination of calcium:

	tan α	Mean deviation, in %
Ca I 4226.728 A – Ir 4210.587 A	1.111	7
Ca II 3968.468 A – IrI 3976.311 A	1.327	6
Ca II 3933.666 A – Ir 3915.384 A	1.0	9

The mean deviation from the curve was determined on the basis of seven negatives for each pair of lines.

As an example we show in Fig. 3 b the curve for the pair of lines Ca 3968.478 A and Ir I 3976.311 A, which has the steepest slope.

The analytical pairs of lines used for magnesium determination were the following:

	tan α	Mean deviation, in %
Mg II 2795.530 A – Ir I 2800.820 A	1.111	6
Mg I 2852.129 A – Ir I 2849.725 A	0.839	13
Mg II 2802.695 A – Ir I 2800.820 A	0.933	11

The best results were obtained on using the first pair of lines. The deviation was calculated as the mean of ten negatives. The curve for the determination of magnesium in iridium is shown in Fig. 3a.

During determination of aluminum in iridium almost equally good results were given by the following pairs of lines:

	tan α	Mean deviation, in %
Al I 3961.527 A – Ir I 3976.311 A	0.679	12
Al 3944.032 A – Ir I 3915.384 A	0.577	14

The curve for the first pair is shown in Fig. 4a. Only one pair of lines, which was suitable for photometric measurements, was used for determination of silicon.

The pair used was Si I 2881.578 A Ir 2880.211A (Fig.4b), the curve obtained for this pair was not steep enough, and many of the silicon lines were not observed at all on the negatives. The mean deviation from the calibration curve amounted to about 20% in this case.

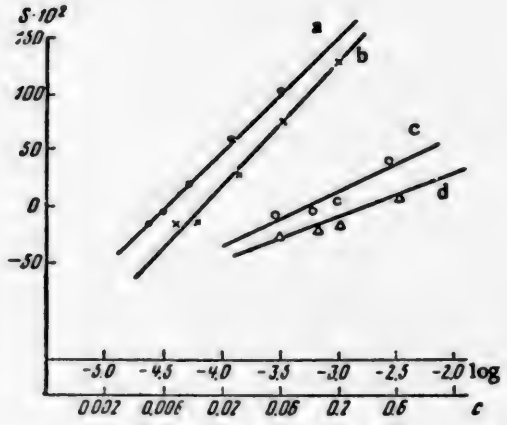

Fig. 3.

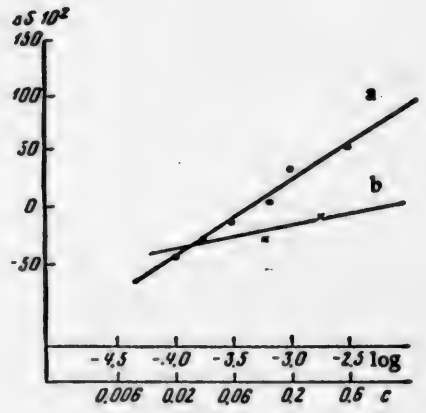

Fig. 4.

The pair of lines Sn I 3034.121 A, Ir I 3032.410A was used fortin determination. This pair gave a curve whose slope was 0.625 while the deviation from the curve amounted to 10% on the average. Another pair of lines Sn 3175.019 A, Ir 3177.582 A was also found to be suitable; in this case, however, the slope of the curve was less (Fig. 3 c, d).

It should be pointed out that the sensitivity for the determination of tin in iridium is not high, and the lower limit of the tin concentration which can be determined is 0.4% with respect to iridium.

SUMMARY

A technique has been developed for the spectrographic determination of calcium, magnesium, aluminum, silicon, and tin in refined rhodium and iridium.

A method is described for the preparation of standard solutions of rhodium and iridium containing small amounts of calcium, magnesium, aluminum, silicon, and tin.

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Received June 26, 1957

THE USE OF THIOSEMICARBAZIDES IN ANALYSIS

COMMUNICATION I. QUANTITATIVE DETERMINATION OF UNI- AND DIVALENT MERCURY BY MEANS OF 1-PHENYLTHIOSEMICARBAZIDE

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Of the methods for determining uni- and divalent mercury, the most widespread are those based on titration with ammonium thiocyanate or sodium chloride [1]. During determination of small amounts of divalent mercury, good results are obtained by titrating with potassium iodide [2]. Iatsimirskii and Astashev [3] have developed a method for determining mercury by means of thiourea. Kuznetsov and Mitrofanova [4] have suggested the determination of gamma amounts of mercury by means of stilboxine. Other methods have been described in the literature, but most of them are only applicable to the determination of univalent or divalent mercury, and do not permit determination of total uni- and divalent mercury. As a result of this, for example, during the determination of univalent mercury by means of a method which is really meant for determination of divalent mercury, it is necessary to oxidize the univalent mercury beforehand, and this step means, in a number of instances, the introduction of complications, and limits the applicability of many methods.

The present article describes results obtained during the application of 1-phenylthiosemicarbazide as a reagent for the quantitative determination of mercury by a titrimetric method based on the reaction: $Hg(NO_3)_2+2C_6H_5NHNHCSNH_2 \rightarrow [Hg(S_6H_5NHNHCSNH_2)_2]^{2+} + 2NO_3^-$. As a result of the insignificant dissociation of the complex $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$ the equilibrium of the reaction shifts almost completely to the right.

As compared with other similar methods, when 1-phenylthiosemicarbazide is used, it is possible to determine both uni- and divalent mercury. The indicator used is a 0.1 N solution of copper nitrate. During the interaction of very dilute solutions of 1-phenylthiosemicarbazide with copper nitrate, sulfate, chloride, or acetate the solution is colored an intense blue color as the result of the formation of a soluble complex:

$$Cu(NO_3)_2 + 2C_6H_5NHNHCSNH_2 \rightarrow [Cu(C_6H_5NHNHCSNH_2)_2]^{2+} + 2NO_3^-.$$

With concentrated solutions of reactants, the solution acquires a dark blue color, and a precipitate may form. On addition of a solution of mercury nitrate to a solution of 1-phenylsemicarbazide and the copper complex $[Cu(C_6H_5NHNHCSNH_2)_2]^{2+}$, there occurs, in the first instance, a reaction between mercury ions and the molecules of 1-phenylthiosemicarbazide. Subsequently, there occurs substitution of copper ions in the complex $[Cu(C_6H_5NHNHCSNH_2)_2]^{2+}$ by Hg ions, with formation of a more stable complex ion $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$. The blue color of the solution thereupon changes to yellow or weak-yellow, depending on the concentration of the solution. Thus, the equivalence point is determined by the color change from blue to yellow. During determination of of univalent mercury is is essential to bear in mind that in a solution of its salts, there exists the equilibrium $[Hg_2]^{2+} \rightleftharpoons Hg^{2+} + Hg$. 1-Phenylthiosemicarbazide, which forms a stable complex $[Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$, with Hg^{2+} ions, displaces this equilibrium to the right: $[Hg_2]^{2+} + 2C_6H_5NHNHCSNH_2 \rightarrow$ $\rightarrow Hg + [Hg(C_6H_5NHNHCSNH_2)_2]^{2+}$. During this reaction fine drops of metallic mercury separate out; in order to eliminate the effect of this mercury on the determination of the equivalence point, the solution of 1-phenylsemicarbazide should be diluted with water at the rate of 75-100 ml of water per ml of an acetic acid solution

of 1-phenylsemicarbazide before carrying out the titration. Under these conditions, the color change of the solution from blue to yellow can be determined fairly accurately, and the liberation of metallic mercury does not affect the accuracy of determination.

The method suggested permits small amounts of univalent and divalent mercury to be determined accurately in dilute solutions of nitrates. Chlorine and bromine ions, however, complicate determination of mercury. In the latter case, the reaction between 1-phenylthiosemicarbazide and mercuric ions is slow, and the color change from blue to yellow is not clear cut.

For the determination of mercury in chlorides or bromides it is essential to convert them first to the nitrate, for which purpose an excess of sodium hydroxide solution is added to the test solution. The precipitated mercury oxides are filtered off, washed with water, and dissolved in nitric acid; the mercury is then determined in the solution thus obtained. Most cations and anions do not interfere with the determination of mercury. Analysis can be carried out in acid media over a wide pH range. In contrast to most other analogous organic compounds, 1-phenylthiosemicarbazide forms a compound with a constant composition with mercury. 1-Phenylthiosemicarbazide which is readily synthesized from ammonium thiocyanate and phenylhydrazine hydrochloride can be recrystallized easily and prepared in a chemically pure form. Its acetic acid solution, which is used for mercury determination, can be stored for long periods without any appreciable change.

When calculating the results one should bear in mind that the gram-equivalent of 1-phenylthiosemicarbazide is equal to its molecular weight. 1 ml of a 0.05 N solution of 1-phenylthiosemicarbazide is equivalent to 5.015 mg of divalent mercury and 10.03 mg univalent mercury.

For the quantitative determination of 1-phenylthiosemicarbazide and other thiosemicarbazides, they are titrated with a solution of mercuric nitrate using copper nitrate as indicator. By using 0.1-0.05 N mercuric nitrate, it is possible to determine macro- and micro-amounts of 1-phenylthiosemicarbazide and other thiosemicarbazides. The mercuric nitrate solution is standardized against an exact aliquot of 1-phenylthiosemicarbazide.

The order in which titration is carried out is of essential importance. During the determination of both thiosemicarbazides and mercury, it is essential that the sclution of mercurous or mercuric nitrate be added to the solution of the thiosemicarbazide.

1-Phenylthiosemicarbazide was prepared from phenylhydrazine hydrochloride and ammonium thiocyanate as follows. 152.24 g of ammonium thiocyanate (2 moles) and 144.5 g (1 mole) of phenylhydrazine hydrochloride were measured out into a 500-ml flask, and the mixture covered with 200 ml of acetic acid. The flask was fitted with a reflux condenser and was heated on a boiling water bath for 2 hours. The contents of the flask were periodically shaken, whereupon the ammonium thiocyanate and phenylhydrazine hydrochloride dissolved completely. Hydrogen sulfide was liberated during the reaction.

250-300 ml of water was added to the solution when heating was finished. The precipitate which separated out on cooling was filtered on a Buchner funnel, washed with water, and then recrystallized from alcohol. The yield of recrystallized product, after drying in a thermostat at 105-110° amounted to 60 g; the melting point was 197-198°. According to published data, the melting point of 1-phenylthiosemicarbazide is 200-201°. The product obtained dissolves readily in alcohol and in acetic acid but is less soluble in water and in benzene.

Synthesis of 1-phenylthiosemicarbazide can be carried out in an aqueous medium by heating the reactants to the boiling point for 2 hours. The yield of the finished product in this instance will be somewhat less. Potassium thiocyanate can be used instead of ammonium thiocyanate.

Standard solutions of 1-phenylthiosemicarbazide (0.04-0.005 N) were prepared by dissolving the exact aliquots of the chemically pure reagent in 70-80% acetic acid on heating in a standard flask. The titer of the solution does not change over a long period of time.

For analysis, the test solution of mercury salt was placed in a standard flask and the volume made up to the mark with water. For this purpose it is necessary that the concentration of the test solution should be 0.1-0.5 N.

An exact amount of the acetic acid solution of 1-phenylthiosemicarbazide was measured out from a macro- or micro-buret; to this solution 2-3 drops of a 0.1 N solution of cupric nitrate was added, after which the solution

of 1-phenylthiosemicarbazide was titrated with mercuric nitrate solution until the color of the solution changed from blue to yellow or weakly yellow.

For the determination of mercurous nitrate, 1-3 ml of the acetic acid solution of 1-phenylthiosemicarbazide was measured out of a micro-buret into a conical flask, and the solution diluted with water on the basis of 75-100 ml of water to each milliliter of 1-phenylthiosemicarbazide. After addition of 0.5-1 ml of 0.1 N cupric nitrate, the contents of the flask were titrated against a standard solution of mercurous nitrate from a micro-buret until the color of the solution changed from blue to a weak grey-yellow.

TABLE 1

Determination of Mercury in $Hg_2(NO_3)_2$

$C_6H_5N_2H_3 \cdot CSNH_2$ taken in mg as a soln.	Water added, in ml	Mercury found, in mg	Mercury taken, in mg
7.0	75	8.39	8.33
7.0	100	8.39	8.35
7.0	150	8.39	8.42
14.0	125	16.77	16.80
14.0	250	16.77	16.85
14.0	200	16.77	16.85

TABLE 2

Determination of Mercury in $Hg(NO_3)_2$

$C_6H_5N_2H_3 \cdot CSNH_2$ taken in mg, as a soln.	Mercury found, in mg	Mercury taken, in mg
70.0	41.93	42.08
70.0	41.93	42.08
105.0	63.08	63.186
140.0	83.86	83.66
140.0	83.86	83.66
35.0	20.46	20.40
35.0	20.46	20.40
14.0	8.38	8.36
14.0	8.38	8.36

The color of the solution changes very sharply on addition of one drop of the test solution in excess. In order to avoid overstepping the endpoint, the solution of mercuric nitrate should be added slowly, with careful stirring of the solution, toward the endpoint.

Silver, chloride, bromide, and quadrivalent tin ions interfere with the mercury determination.

The results obtained are given in Tables 1 and 2.

SUMMARY

1. A method has been developed for the quantitative determination of uni- and divalent mercury, by titration with 1-phenylthiosemicarbazide in the presence of cupric salts as indicator.

2. A method is suggested for the quantitative determination of 1-phenylthiosemicarbazide and other thiosemicarbazides by titration with mercuric nitrate.

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Received April 25, 1957

*Original Russian pagination. See C.B. Translation.

DIALKYL- AND DIARYLDITHIOPHOSPHORIC ACIDS AS ANALYTICAL REAGENTS

COMMUNICATION 4. SEPARATION OF CADMIUM FROM ZINC AND OTHER ELEMENTS. GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF CADMIUM*

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It has been pointed out before [1-2] that diethyldithiophosphoric acid $(C_2H_5O)_2PSSH$ and its soluble salts, as well as other dithiophosphates quantitatively precipitate a number of heavy metals, many of which give sparingly soluble sulfides. In general, the dithiophosphates are reminiscent in their properties of the dithiocarbamates which are widely used in analytical practice, and also of the xanthogenates, but they differ from them in exhibiting greater selectivity. Thus, the dithiophosphates do not precipitate elements of the third analytical group, including zinc. The exception is trivalent iron which, at a certain hydrochloric acid concentration, forms a black precipitate. At the same time, cadmium belongs to the number of those elements which form sparingly soluble compounds with dialkyl- and diaryldithiophosphates. This opens up the possibility of developing a method for the quantitative separation of cadmium from zinc, and also from other elements of groups I, II, and III.

Separation of cadmium from zinc is of great practical importance, since both these elements often occur together in natural and industrial products, while at the same time there is a real need for simple, rapid, and accurate methods for separating cadmium from zinc, which would satisfy the requirements of production control. Serious difficulties have been caused by the absence of selective reactions for cadmium and zinc. The close similarity between the chemical properties of cadmium and zinc seriously limit the possibilities of developing methods for their separation, and of developing methods for determination of cadmium in the presence of zinc. A review of methods for determining cadmium, and for separating it from zinc and other elements is to be found in the well-known textbook of Fresenius and Jander [4]. Most of the gravimetric [5-9], titrimetric, and other methods for determining cadmium, assume that zinc is absent. There are a number of methods at present for separating cadmium from zinc, and for the determination of cadmium in the presence of zinc. Cadmium can be separated from zinc and some other elements by precipitation with hydrogen sulfide from acid solution [4], or by precipitation with thiourea from an alkaline cyanide solution [10]; precipitation of cadmium by means of Reinecke's salt in the presence of thiourea is widely used, the cadmium is precipitated as $[Cd(CSN_2H_4)_2][Cr(SCN)_4(NH_3)_2]$[11-14]. Precipitation of cadmium by means of 2-(o-hydroxyphenyl)-benzoxazole from an alkali solution containing tartrate permits quantitative separation of cadmium from zinc and other elements [15]. For determination of cadmium in the presence of zinc, methods have been developed which are based on the precipitation of the complex anions $[CdI_4]^{2-}$ or $[CdBr_4]^{2-}$ by organic bases. The precipitates obtained are weighed. Titrimetric or photometric finishes for the determination of cadmium are much rarer. β-Naphthoquinoline [16-18], methyl violet [19], brucine [20], and other materials have been used as precipitants for the anion $[CdI_4]^{2-}$, while brucine [21, 22], antipyrine [23, 24], diantipyrylmethane [25], and diantipyrylorthohydroxyphenylmethane [26] have been used for precipitating $[CdBr_4]^{2-}$. There are methods for separating cadmium and zinc based on ion exchange [27-29], and by means of activated metallic copper [30]; in the latter method, the metallic copper removes cadmium from a cyanide solution containing tartrate, while all the zinc remains in solution. Cadmium can be very conveniently determined in the presence of zinc by a polar-

* For Communication 3, see [3].

ographic method [31-43]. This method is very often used for production control. Relatively reliable results are obtained during the separation of zinc and cadmium, and during their determination in each others presence by the method of internal electrolysis [44-45], by fractional titration with amalgam [46], by deposition of cadmium on an aluminum cathode [47], or by electrolysis with a mercury electrode [48]. Of other methods for separating cadmium and zinc, and for determining cadmium in the presence of zinc, mention may be made of the potentiometric ferrocyanide method [49], and the potentiometric xanthogenate method [50].

During precipitation of cadmium with hydrogen sulfide or thiourea, coprecipitation of zinc occurs; in order to get more reliable results, precipitation has to be repeated. The Reineckate method has some essential advantages over the sulfide and some other methods; accordingly, it has received fairly wide application in practice during production control, although it is not free from drawbacks. Songina [14] has shown that the composition of the precipitate obtained in practice does not accurately correspond to the formula $[Cd(CSN_2H_4)_2][Cr(SCN)_4(NH_3)_2]_2$. Thus, in order to calculate the amount of cadmium, an empirical factor is employed which has to be determined for each batch of Reinecke's salt. The other chemical methods have not been widely used, mainly because of the fact that the reagents are not readily available or because of the rather complex procedures involved.

The search for new methods of separating cadmium from zinc, and for methods of determining cadmium quantitatively in the presence of zinc is of undoubted practical interest.

EXPERIMENTAL

Reagents and Apparatus

1. Standard solutions of cadmium sulfate were prepared by dissolving the exact amounts of analytical grade material. The solutions were standardized by precipitating the cadmium with anthranilic acid and weighing the precipitate obtained [4].

2. The 0.05 solution of nickel diethyldithiophosphate used as precipitant $[(C_2H_5O_2)PSS]_2Ni$ was prepared by dissolving the purified preparation in water. The synthesis and purification of nickel diethyldithiophosphate have been described earlier [1]. Other nickel dialkyl- and diaryldithiophosphates have been synthesized by similar methods [3]. Potassium diethyldithiophosphate was also used in the course of the work.

3. Standard iodine and sodium thiosulfate solutions were prepared by the usual methods. The sulfates, nitrates, and chlorides of group I, II, and III metals, used in the course of the work, were either analytical grade or pure grade materials, and were used without additional purification.

The Properties of Cadmium Dialkyl- and Diaryldithiophosphates

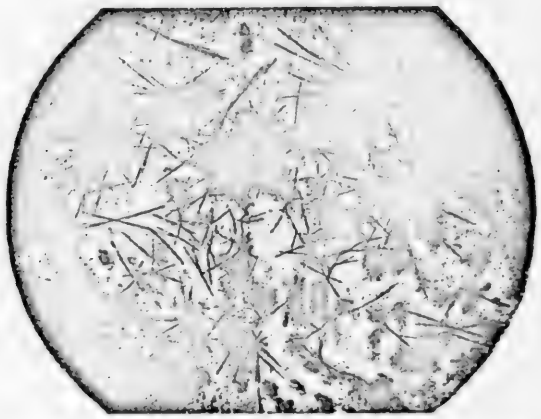
Cadmium dialkyl- and diaryldithiophosphates separate out as white, flocculent, crystalline precipitates on addition of the appropriate dialkyl- or diaryldithiophosphate in the form of the nickel or potassium salt to a solution of cadmium sulfate. Changes in the concentration of sulfuric and nitric acids over a wide range (from 0 to 6 moles/liter) have almost no effect on precipitation of cadmium. The reason is that the dialkyl- and diaryldithiophosphoric acids are strong acids; titration curves for solutions of diethyldithiophosphoric acid and sulfuric acid with KOH of the same molarity are almost identical to one another, both with respect to shape, and the value of the jump at the equivalence point. At high concentrations of nitric acid in the solution from which precipitation is to be effected, oxidation of the anion of the dithiophosphoric acid to the disulfide occurs. At mineral acid concentrations in excess of 6 moles/liter, signs can be observed of the decomposition of the dithiophosphoric acid.

The cadmium precipitates formed are almost insoluble in solutions of strong mineral acids, but readily dissolve in organic solvents which are immiscible with water (in the presence of dilute acids) to form colorless solutions; they also dissolve in ammonia.

Under the microscope (magnification 80) cadmium diethyldithiophosphate shows up in the form of characteristic needle-shaped crystals (Fig.) which permit cadmium to be detected microcrystalloscopically in the presence of ions of Group I, II, and III and also of some Group IV ions. When excess reagent is used, cadmium can be detected in the presence of 100 times its amount of copper, lead, and bismuth, at a dilution (relative to cadmium) of 1:50,000. The limiting dilution when the test is carried out in a test-tube is 1:150,000.

Cadmium diethyldithiophosphate melts at 144°.

Cadmium diethyldithiophosphate, after washing with water and drying in air to constant weight, was analyzed by the method described previously [2]. Results of numerous determinations of cadmium in the form of its anthranilate, of sulfur as barium sulfate, and of phosphorus as magnesium pyrophosphate – these results have been left out for the sake of brevity – as well as results of the iodometric titration of the precipitate (Table 1), and the result of numerous determinations of cadmium by weighing as the diethyldithiophosphate



Crystals of cadmium diethyldithiophosphate precipitate.

(some of these results are given below), demonstrate convincingly that the composition of the precipitate corresponds to the formula $[(C_2H_5O)_2PSS]_2Cd$.

The approximate solubility of cadmium diethyldithiophosphate in water was determined by evaporating a known volume of the saturated solution and weighing the residue. The saturated solution was prepared by periodically shaking 1-2 g of the freshly prepared, thoroughly washed preparation with 4 liters of distilled water at room temperature (18-20°). The solution obtained was filtered, and 1 or 2 liters of the filtrate evaporated in a large beaker on a water bath of a volume of 4-5 ml, the beaker being shielded so that no dust got in. On evaporation to this volume, large, well-formed, needle-shaped crystals of cadmium diethyldithiophosphate separated out; these were filtered through a porcelain micro-crucible dried beforehand at 105°. The saturated aqueous solution of cadmium diethyldithiophosphate was used for transferring the crystals quantitatively to the crucible. The crucible plus precipitate were dried at 105° to constant weight. The melting point was then determined in order to make sure that no decomposition of the material had occurred during the process of prolonged evaporation. In all cases the melting point was 144°; thus cadium diethyldithiophosphate does not undergo any appreciable decomposition under the experimental conditions used.

TABLE 1

Iodometric Titration of Cadmium Diethyldithiophosphate*

Sample wt., in g	Found, in g	Error	
		Absolute, in g	Relative, in %
0.1649	0.1657	0.0008	+0.5
0.2020	0.2026	0.0006	+0.3
0.2344	0.2340	0.0004	−0.4

*The precipitate was dissolved in concentrated hydrochloric acid and 2-3 ml of CCl_4 added, this was followed by an equal volume of water and an excess of a standard iodine solution; the solution was then slowly titrated with sodium thiosulfate. For the reaction between iodine and diethyldithiophosphate see [1]. The amount of precipitate was calculated on the basis of the formula $[(C_2H_5O)_2PSS]_2Cd$.

Table 2 contains the results obtained.

Saturation is only attained after 20-25 days. Saturation is reached more rapidly by shaking more often. The solubility of cadmium diethyldithiophosphate can be regarded as being equal to 0.118 g in 1 liter of water at 18-20°, or 2.4×10^{-4}

mole/liter. The solubility product:

$$L_s\ [(C_2H_5O)_2PSS]^- \cdot [Cd^{2+}] = 5.8 \cdot 10^{-11}.$$

A similar value for the solubility of cadmium diethyldithiophosphate in water was found by V. M. Byrko [51] using a radiometric method.* The solubility of cadmium diethyldithiophosphate drops sharply in the presence of excess precipitant, but it is still high enough to lead to low results during the gravimetric determination of cadmium.

TABLE 2

Determination of the Solubility of Cadmium Diethyldithiophosphate in Water at 18-20°

Period of saturation, in days	8	10	30	60	90
Concentration, in g/liter	0.0303	0.0640	0.117	0.117	0.121

Cadmium diethyldithiophosphate satisfies the basic requirements of a precipitate suitable for gravimetric determination. Cadmium can be almost quantitatively precipitated from solution as the diethyldithiophosphate when it is precipitated from relatively small volumes by means of excess precipitant. In this way the error resulting from the solubility of the precipitate drops from 0.1-0.2 mg (the limit of the sensitivity of the analytical balance). It is necessary to wash the precipitate with a saturated aqueous solution of cadmium diethyldithiophosphate, and not with distilled water or a 1% solution of ammonium nitrate. When a precipitate is washed with portions of water during determination of 0.0020-0.04 g of cadmium, the results were always low by 3-5%. Precipitation of cadmium with diethyldithiophosphate is fairly specific. A very important fact is that zinc is not precipitated even when present in appreciable concentrations. Divalent iron, aluminum, gallium, nickel, cobalt, chromium, manganese, the alkaline-earth elements, and the alkali metals also remain in solution. Other ions (at any concentration) do not prevent formation of the precipitate of cadmium diethyldithiophosphate. After washing, the precipitate is almost free of foreign ions; thus coprecipitation is expressed only to a very weak degree. The precipitate is readily filtered and washed. Cadmium, in addition to being separated quantitatively, can be weighed as its diethyldithiocarbamate, since this compound after drying at room temperature, or at 105°, has a strictly defined composition corresponding to the formula $[(C_2H_5O)_2PSS]_2Cd$ (the conversion factor to cadmium is 0.2328). The cadmium compound is completely stable to washing and drying, it is not appreciably hygroscopic, and does not lose weight during drying.

For the gravimetric determination of cadmium, 0.05 M nickel or potassium diethyldithiophosphate solution in an excess of one and a half or twice the amount of cadmium, is added to 10-100 ml of a nitric or sulfuric acid solution containing 0.002-0.1 g of cadmium, as well as zinc and other metals (in the form of chlorides for example); the precipitate formed is allowed to stand in the solution for several minutes, after which it is filtered off through a tared No. 3 sintered glass filter; the precipitate is then washed with small portions of a saturated aqueous solution of cadmium diethyldithiophosphate until the washings give a negative reaction for nickel with dimethylglyoxime (after addition of ammonia); the precipitate is finally dried to constant weight at 105°. Results of such determinations are given in Table 3.

For the accurate determination of small amounts of cadmium, a titrimetric method, based on the oxidation of the organic component of the precipitate of cadmium diethyldithiophosphate by means of iodine in a strongly alkaline medium, is very convenient.

The precipitate of cadmium diethyldithiophosphate which has been filtered through a No. 3 glass crucible and washed with small portions of water 3-4 times, is treated on the filter with 6 N sodium hydroxide in

* For results on the determination of the solubility of cadmium diethyldithiophosphate in the presence of ions of diethyldithiophosphoric acid at various ionic strengths, see [5].

order to break down the diethyldithiophosphate, and to create a strongly alkaline medium. The amount of alkali taken is such that after addition of iodine solution, the alkali concentration in the final solution is

TABLE 3

Determination of Cadmium by Precipitating and Weighing as $[(C_2H_5O)_2PSS]_2Cd$

Taken, in g		Found, in g		Error	
Cd	salt	CdR_2	Cd	Absolute, in g	Relative, in %
0.0431	1.5 $ZnSO_4 \cdot 7H_2O$	0.1847	0.0429	—0.0002	—0.4
0.4331	1.5 $ZnSO_4 \cdot 7H_2O$	0.1850	0.0430	—0.0001	—0.2
0.0431	1.5 $MgSO_4$	0.1847	0.0430	—0.0001	—0.2
0.0431	1.5 $MgSO_4$	0.1852	0.0431	0	0
0.0431	1.5 $Cr_2(SO_4)_3$	0.1835	0.0427	—0.0004	—0.9
0.0258	2 $Al(NO_3)_3$	0.1107	0.0257	—0.0001	—0.2
0.0258	1.5 $Fe_2(SO_4)_3$	0.1102	0.0256	—0.0002	—0.4
0.0258	2 $CoSO_4$	0.1101	0.0256	—0.0002	—0.4
0.0258	1.5 $Ni(NO_3)_2$	0.1104	0.0256	—0.0002	—0.4
0.0431	1.5 Na_2SO_4	0.1847	0.0429	—0.0002	—0.4
0.0431	1.5 KNO_3	0.1845	0.0429	—0.0002	—0.4
0.0431	1.5 NH_4NO_3	0.1853	0.0430	—0.0001	—0.2
0.0258	2 KCl	0.1103	0.0256	—0.0002	—0.4

0.5-1.5 N. Excess standard iodine solution is added; after 5-10 minutes the solution is acidified with sulfuric acid until the solution gives a weakly acid reaction with universal indicator paper; excess iodine is titrated with thiosulfate. Calculations are based on the equation:

$$[(C_2H_5O)_2PSS]_2Cd + 16I_2 + 42NaOH = 2(C_2H_5O)_2POONa + 4Na_2SO_4 + 32NaI + Cd(OH)_2 + 20H_2O$$

The method described for the separation of cadmium from zinc and other elements, and for the gravimetric determination of cadmium gives completely satisfactory results. Changes in hydrochloric acid concentration over a wide range do not have appreciable effects on the results of cadmium determination. The method of drying the precipitate of cadmium diethyldithiophosphate (drying to constant weight in air at 105°, and over sulfuric acid) has little effect on the experimental results. Appreciable amounts of zinc, nickel, cobalt, aluminum, chromium, iron, magnesium, beryllium, the alkaline-earths, and the alkali metals do not interfere with cadmium determination. Heavy metals which are precipitated by diethyldithiophosphoric acid in an acid medium interfere.

TABLE 4

Determination of Cadmium by Oxidation of the Organic Component of the Diethyldithiophosphate Precipitate by Iodine in a Strongly Alkaline Medium

Cadmium taken, in mg	Cadmium found, in mg	Error	
		in mg	in %
11.24	11.21	—0.90	0.3
5.62	5.65	—0.03	0.5
0.562	0.562	0	0
0.562	0.550	—0.012	2

On the basis of the method described for the separation of cadmium from zinc and other elements, and of the methods for the gravimetric and titrimetric determination of cadmium, it is easy to develop simple, rapid, and accurate analytical methods which would be applicable to various natural and industrial materials, and for production control [52]. Potentiometric titration of cadmium with a solution of nickel diethyldithiophosphate by means of a platinum electrode covered with mercury, is accompanied by a hardly perceptible potential jump at the equivalence point, accordingly, such a method is of no practical importance. Amperometric titration in a supporting electrolyte of various salts (with a mercury electrode, and on the basis of the current obtained by the reduction of cadmium) did not give satisfactory results either.

Direct photometric determination of cadmium as its diethyldithiophosphate is impossible, since this compound in chloroform or carbon tetrachloride starts to absorb light appreciably only at 295 mμ and lower,

and at relatively high concentrations. Preliminary tests showed that it is possible to develop a photometric determination of cadmium, by converting its diethyldithiophosphate into the intensely colored copper diethyldithiophosphate and measuring the optical density of a solution of the latter in an organic solvent. It has been established that cadmium diethyldithiophosphate, on being dissolved in chloroform or carbon tetrachloride, interacts with cupric sulfate in aqueous solution (on shaking):

$$[(C_2H_5O)_2PSS]_2Cd + Cu^{2+} = [(C_2H_5O)_2PSS]_2Cu + Cd^{2+}.$$

SUMMARY

Cadmium diethyldithiophosphate $[(C_2H_5O)_2PSS]_2Cd$ answers all the requirements for a cadium compound which is readily precipitated, and is suitable for the gravimetric determination of this metal. A fairly rapid method has been developed for the gravimetric determination of cadmium in the presence of zinc, and also in the presence of nickel, cobalt, manganese, aluminum, iron, chromium, magnesium, the alkaline-earths, and the alkali metals. The method should find application for the analysis of natural and industrial products.

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Received October 10, 1956.

*Original Russian pagination. See C.B. Translation.
**In Russian.

THE USE OF SODIUM PARA-AMINOBENZOATE FOR THE TITRIMETRIC DETERMINATION OF CADMIUM

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Despite the existence of a considerable number of methods for the quantitative determination of cadmium [1-7], analysts frequently have to resort to the gravimetric sulfate method which, although characterized by accuracy, is very long and is not suitable for the determination of cadmium in a mixture of cations. In recent years complexometric methods of determining cadmium have become increasingly important.

During a study of the effect of substituents on the solubility of the benzoates, it was found that cadmium salts form a sparingly soluble compound with sodium para-aminobenzoate. This fact served as a basis for developing a quantitative method of determining cadmium. Essentially the method consists of the preliminary precipitation of cadmium by means of sodium para-aminobenzoate, and the subsequent bromatometric determination of cadmium in the precipitate on the basis of the para-aminobenzoic acid.

Before establishing the conditions for carrying out the method, the composition of the precipitate obtained by precipitating cadmium with sodium para-aminobenzoate was determined.

The precipitate was prepared by precipitating cadmium from a 0.3 M solution of cadmium acetate with a threefold excess of sodium para-aminobenzoate. The precipitate was washed 4 times with water, and dried at 120° to constant weight (this temperature ensures preparation of the anhydrous salt). Well known analytical

TABLE 1

Wt. of prec., in g	$CdSO_4$ found, in g	Cd found	
		in g	in %
0.5160	0.2774	0.1501	29.0
0.5086	0.2714	0.1463	28.8
0.5010	0.2668	0.1439	28.7
0.5174	0.2780	0.1499	29.0
0.4978	0.2678	0.1444	29.0
		Mean	28.9

TABLE 2

Wt. of prec., in g	Para-aminobenzoic acid found	
	in g	in %
0.5088	0.3607	70.9
0.5076	0.3568	70.3
0.5080	0.3687	70.6
0.5052	0.3568	70.6
0.4154	0.2936	70.7
	Mean	70.6

reactions were used for detecting cadmium ions and para-aminobenzoic acid in the precipitate. Cadmium was determined quantitatively in the precipitate by dissolving an aliquot of the precipitate, which had been heated to constant weight at 120°, in 0.8 N sulfuric acid; the cadmium was then precipitated with hydrogen sulfide and determined gravimetrically as the sulfate [8]. The results of these determinations are given in Table 1.

For the quantitative determination of para-aminobenzoic acid, the exact amount of the product dried to a constant weight was dissolved in 1 N hydrochloric acid in a 100-ml standard flask. The para-aminobenzoic acid was determined bromatometrically in 25 ml of this solution. The results of these determinations are given in Table 2.

Found	28.9% Cd and 70.6% n-$H_2NC_6H_4COOH$
Calculated for $(H_2NC_6H_4COO)_2Cd$	29.2% Cd and 70.8% n-$H_2NC_6H_4COOH$

Results for the determination of the water of crystallization showed that cadmium para-aminobenzoate crystallizes with three molecules of water. Thus, the precipitate obtained during the interaction of cadmium salts with sodium para-aminobenzoate has the following composition:

$$(H_2NC_6H_4COO)_2Cd \cdot 3H_2O.$$

In order to study the effect of the amount of precipitant on the results of the cadmium determinations, precipitation was produced by various amounts of 0.3 M sodium para-aminobenzoate in 10 ml of cadmium acetate (0.003709 g Cd in 1 ml). After standing for 10 minutes the precipitate was filtered and then washed 4 times with water. The precipitate was dissolved in 50 ml 1 N hydrochloric acid, and the cadmium determined bromatometrically on the basis of para-aminobenzoic acid.

The results of these experiments are given in Table 3.

TABLE 3

(0.03709 g Cd taken)

Am't of 0.3 M sodium para-aminobenzoate, in ml	Molecular ratio of Cd to sodium para-aminobenzoate	Cd found, in g	Difference, in Cd, in g
1.5	1 : 1.3	Insignificant deposition of precipitate	
2.5			
3	1 : 2.2	0.03163	—0.00546
4	1 : 2.6	0.03373	—0.00336
5	1 : 3.5	0.03624	—0.00085
10	1 : 4.4	0.03624	—0.00085
25	1 : 9	0.03639	—0.00070
	1 : 22	0.03653	—0.00056

Thus, precipitation of cadmium starts at a molar ratio of cadmium to sodium para-aminobenzoate of 1 : 1.3. Complete precipitation is achieved at a ratio of 1 : 3.5. Excess of reagent has no effect on the accuracy of the results obtained.

In order to determine the time necessary for formation of the precipitate, 25 ml of a 0.3 M solution of sodium para-aminobenzoate was added to 20 ml of cadmium acetate solution containing 0.007200 g Cd per ml. The precipitates were allowed to stand for various time intervals. Cadmium was then determined in the precipitates by the method described above.

These tests showed that the length of time for which the precipitate is allowed to stand has no effect on the accuracy of the results. The precipitate settles out completely in the course of 10-15 minutes, and is readily filtered.

In order to study the loss of cadmium on washing with water, cadmium was precipitated from 20 ml of a solution of cadmium acetate (0.007200 g Cd per ml) by 25 ml of 0.3 M sodium para-aminobenzoate. After ten minutes standing the precipitate was transferred to a filter and washed with water. 4-6 ml of water was used for each washing, the precipitate was finally dissolved in 50 ml of 2 N HCl in a 100-ml standard flask and the volume made up to the mark with water. Cadmium was then determined bromatometrically in 25 ml of this solution.

The results of these experiments are given in Table 4.

These results show that low values are obtained when the precipitate is washed repeatedly with water. Washing with 70° alcohol gives completely acceptable results (Table 5).

Precipitation of cadmium is quantitative in the pH range 2-6.5.

The experimental results obtained enabled us to develop a method for the titrimetric determination of cadmium by means of sodium para-aminobenzoate.

An aliquot of the cadmium salt (0.1-0.15 g Cd) was dissolved in 15-20 ml of water, 25 ml of 0.3 M sodium para-aminobenzoate was added and the precipitate formed allowed to stand for 10-15 minutes. The precipitate was then transferred to a filter and washed 4-5 times with 70° alcohol. The precipitate was washed off the filter by means of 20-30 ml of 2 N hydrochloric acid into a 100-ml standard flask, and the volume made up to the mark with water. To 20-25 ml of this solution, contained in a flask, was added 25-30 ml of 1 N hydrochloric acid, followed by 0.5 g of potassium bromide; then 0.1 N $KBrO_3$ solution was added until the yellow color of bromine was observed; 5 ml of $KBrO_3$ solution was then added in excess. The whole was thoroughly mixed and 0.1 N arsenious acid added until the yellow color disappeared. Excess arsenious acid was titrated with potassium bromate in the presence of indigo carmine or methyl orange.

TABLE 4

(0.1440 g Cd taken)

No. of water washes	Cd found, in g	Difference in Cd, in g
3	0.1467	+0.0027
4	0.1427	—0.0013
5	0.1416	—0.0024
6	0.1414	—0.0026
10	0.1393	—0.0046

TABLE 5

(0.1440 g Cd taken

No. of alcohol washes	Cd found, in g	Difference in Cd, in g
3	0.1469	+0.0029
4	0.1457	+0.0017
5	0.1435	—0.0005
6	0.1435	—0.0005
10	0.1435	—0.0005

TABLE 6

Wt. of Cd $(CH_3COO)_2$, in g	Cd found in g	Cd found in %	Wt. of $Cd(CH_3COO)_2$, in g	Cd found in g	Cd found in %
0.2844	0.1205	42.36	0.2073	0.0873	42.57
0.3190	0.1354	42.43	0.3030	0.1289	42.55
0.3052	0.1289	42.33	0.3012	0.1276	42.36
0.4738	0.2006	42.37	0.4014	0.1698	42.32
0.4804	0.2036	42.39	0.4236	0.1788	42.22
	Mean	42.37		Mean	42.40

TABLE 7

Cd taken, in g	Cd found in g	Difference in Cd in g	Difference in Cd in %
	Cadmium iodide		
0.0498	0.05001	0.00021	+0.4
0.0498	0.05058	0.00078	+1.5
0.0498	0.05001	0.00021	+0.4
	Cadmium chloride		
0.1242	0.1234	0.0008	—0.6
0.1242	0.1228	0.0014	—1.1
0.1242	0.1237	0.0005	—0.4
	Cadmium nitrate		
0.1064	0.1062	0.0002	—0.2
0.1064	0.1056	0.0008	—0.8
0.1064	0.1059	0.0005	—0.5

TABLE 8

(0.1440 g Cd taken)

Zn taken, in g	Cd found, in g	Difference in Cd, in g
0.07	0.1430	—0.0010
0.07	0.1422	—0.0018
0.07	0.1430	—0.0010
0.7	0.1435	—0.0005
0.7	0.1435	—0.0005
0.7	0.1430	—0.0010

1 ml of 0.1 N $KBrO_3$ corresponds to 0.001405 g Cd.

Using this method, the cadmium content of cadmium acetate (analytical grade GOST 7385/539 was determined. Cadmium was also determined gravimetrically in the same salt by the sulfate method.

The results given in Table 6 show that the accuracy of the proposed method lies within the limits of accuracy of the gravimetric sulfate method. We also checked on the possibility of using this method for other cadmium salts (the nitrate, chloride, and iodide). For this purpose solutions of these salts were prepared and their cadmium content determined both gravimetrically and by the proposed method.

The results obtained are given in Table 7. They show that the method suggested can be used for the determination of cadmium in its acetate, nitrate, chloride, and iodide.

Determination of Cadmium in the Presence of Zinc

During a study of the solubility of the substituted benzoic acids it was found that zinc is not precipitated by sodium para-aminobenzoate. For the determination of cadmium in the presence of various amounts of zinc, solutions of zinc acetate of known concentration were prepared. Known amounts of the zinc acetate solution were added to a cadmium acetate solution (the cadmium concentration was established gravimetrically). Cadmium was then determined quantitatively in this mixture by the method described above. The results obtained are given in Table 8.

This table shows that satisfactory results can be obtained during the determination of cadmium in the presence of zinc at a cadmium to zinc ratio of up to 1:5.

SUMMARY

A new titrimetric method has been developed for the determination of cadmium in the presence of zinc.

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Received July 14, 1956

A NEPHELOMETRIC DETERMINATION OF ZINC BY MEANS OF DIANTIPYRYLMETHYLMETHANE

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Some pyrazolone derivatives, in particular diantipyrylmethylmethane, are very sensitive reagents for zinc in the form of $[Zn(SCN)_4]^{2-}$ (under certain conditions). This anion gives sparingly soluble compounds with many organic cations of the ammonium type, for example benzoquinoline ($C_{13}H_9NH^+$), pyramidone ($C_{13}H_{17}ON_2H^+$) [2]. Iatsimirskii [3] has established that for precipitating anions with large ionic radius one should use cations with fairly large radii. Kuznetsov [4] has found solid phase reactions for $[Zn(SCN)_4]^{2-}$ with colored organic bases.

The present article contains a description of the synthesis and properties of the tetrathiocyanato zincate of diantipyrylmethylmethane; the optimum conditions for the nephelometric determination of zinc by means of this reagent are also described.

Preparation of Diantipyrylmethylmethane Tetrathiocyanatozincate

This compound was prepared by the interaction of 0.5 N zinc chloride, 2 N ammonium thiocyanate, and a 2% alcoholic solution of diantipyrylmethylmethane acidified with hydrochloric acid. Equal volumes of all three solutions (100 ml each) were poured together and the mixture heated almost to the boiling point. On cooling, a precipitate separated out which was recrystallized from alcohol acidified with hydrochloric acid.

Analysis of the compound prepared

0.1960 g of material; 0.0268 $Zn_2P_2O_7$
0.1864 g of material; 0.0254 $Zn_2P_2O_7$
0.0916 g of material; 0.0544 AgSCN
0.0906 g of material; 0.0534 AgSCN

Found %: Zn 5.87; 5.85; SCN 20.78, 20.62. Calculated %: Zn 5.91; SCN 21.08.

The analytical results indicat d that the reaction can be written as follows:

$$2C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2 + ZnCl_2 + 2HCl + 4NH_4SCN =$$
$$= [C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2H]_2[Zn(SCN)_4] + NH_4Cl.$$

The properties of this compound are listed in Table 1.

A characteristic of this compound is its capacity to form a stable turbidity in very dilute aqueous solutions. On the basis of the properties of this compound, a photonephelometric method of determining zinc was developed. The sensitivity of this reagent for the detection of zinc is 0.09 μg of Zn/ml.

Photonephelometric Determination of Zinc

1. Preparation of Diantipyrylmethylmethane Hydrochloride [5]. 5 g of antipyrine was dissolved in a small amount of water, and 1-2 ml of hydrochloric acid sp. gr. 1.19, and 1-2 ml of acetaldehyde added. The

mixture was heated on a water bath for 30-40 minutes, when a crystalline mass was formed. The material was recrystallized from water. It was finally dried in a desiccator.

TABLE 1

Properties of $[C_{11}H_{11}ON_2 \cdot CH(CH_3) \cdot C_{11}H_{11}ON_2 \cdot H]_2[Zn(SCN)_4] + NH_4Cl$

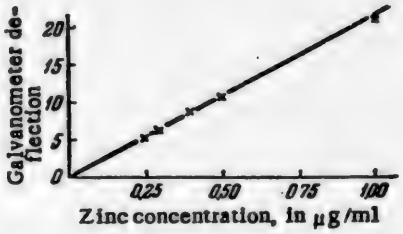
Color	White
Solubility	
In water at 15°	0.12 : 100
In alcohol at 15°	0.15 : 100
In ether at 15°	Insoluble
Behavior with $FeCl_3$	One drop of $FeCl_3$ solution gives a red color of $Fe(SCN)_3$
Behavior with $AgNO_3$	A white precipitate of AgSCN is formed in a nitric acid medium
Behavior with $K_4[Fe(CN)_6]$	A white precipitate $K_2Zn_3[Fe(CN)_6]_2$ is formed
Behavior with NaOH	No precipitate formed
Melting point	127-129°

2. Preparation of a Solution of the Reagent. 1.52 g of ammonium thiocyanate was dissolved in 99 ml of twice-distilled water. To this solution was added, with stirring, 1 ml of a 2% alcoholic solution of diantipyrylmethylmethane; when this was done, a weak turbidity sometimes developed; this was removed by filtering the solution through a normal filter.

TABLE 2

Relation between Zinc Concentration of the Solution and the Galvanometer Readings

Test no.	Zinc conc. in μg Zn in 1 ml test solution	Galvanometer deflection
1	0.25	5.5
2	0.40	9.0
3	0.50	11.0
4	0.70	15.0
5	1.00	21.2



Relation between zinc concentration of the solution and galvanometer readings.

3. Determination of Zinc in Diantipyrylmethylmethane Solutions. Into one cell of a Bendt type photocolorimeter was placed 5 ml of test solution, 0.25 ml of 1 N hydrochloric acid, 0.75 ml of water, 0.03 g of ascorbic acid, 0.05 g of thiourea, and 9 ml of reagent, while a control solution was poured into the other cell.

TABLE 3

Ions	Conc. of ions, μg per ml Solutions			
	№ 1	№ 2	№ 3	№ 4
Magnesium	90	—	9	—
Aluminum	19	—	1.9	—
Copper	1	1	—	—
Iron Fe^{3+}	—	10	—	—
Manganese	—	—	100	10

On the basis of the results obtained (Table 2), a curve relating zinc concentration to galvanometer readings was drawn (Fig).

Four solutions were prepared for the determination of zinc in the presence of Mg^{2+}, Al^{3+}, Cu^{2+}, Fe^{3+}, and Mn^{2+} (Table 3). The zinc concentration was varied over the range 0.25 μg to 1.0 μg per ml.

The reagent solution did not give a turbidity with solutions of the ions indicated in Table 3 over a period of several hours. The experimental conditions used for the

determination of zinc in the presence of these metals were the same as those in the previous experiments. Results of these determinations are given in Table 4.

The presence of Group I and II cations does not interfere with zinc determination; manganese (100 μg), copper (1 μg), nickel, and cobalt (5 μg each) per ml of solution do not interfere. At low concentrations, ferric

TABLE 4

Determination of Zinc in the Presence of Other Metals (10 ml of each of the solutions given in Table 3 were taken)

Test no.	Zinc conc. of test soln., μg per ml	Zinc content found μg per ml	Expt. error, μg per ml	Test no.	Zinc conc. of test soln., μg per ml	Zinc content found μg per ml	Expt. error, μg per ml
1	0.25	0.27	+0.02	6	0.25	0.24	−0.01
2	0.75	0.73	−0.02	7	0.50	0.53	+0.03
3	1.00	1.01	+0.01	8	1.00	1.02	+0.02
4	0.25	0.24	−0.01	9	0.25	0.27	+0.02
5	0.75	0.73	−0.02	10	0.75	0.73	−0.02

iron is reduced to the divalent state by means of ascorbic acid or hydroquinone. Cupric ions are converted into a colorless complex with thiourea when they are present in amounts greater than 1 μg per ml.

The method described has been used for the analysis of alloys, tap water, and spring water.

Determination of Zinc in Alloys

0.1 g of the alloy "elektron" containing 85% Al, 14.17% Mg, 0.29% Mn, 0.08% Cu, and 0.46% Zn was dissolved in a few ml of hydrochloric acid sp.gr 1.03 contained in a quartz beaker. When solution was complete, the liquid was transferred to a 1-liter standard flask. The solution was made up to the mark with twice-distilled water. For the zinc determination 5 ml of this solution was taken, and 0.25 ml of 1.0 N HCl, 0.03 g of ascorbic acid, 0.05 g of thiourea, and 9 ml of reagent solution added to it. After standing for 15 minutes the solution was transferred to the photocolorimeter cell. The other cell was filled with control solution (this solution contained all the components listed above but contained 5 ml of water instead of test solution). The following results were obtained in a series of tests in which zinc was added to the test solutions (Table 5).

TABLE 5

Determination of Zinc in the Alloy "Elektron" (composition 85% Al, 14.17% Mg, 0.46% Zn, 0.29% Mn, 0.08% Cu; sample weight 0.1 g)

Zn content of alloy, mg	Zinc added, mg	Total zinc found, mg	Theor. Zn content, mg	Error, in mg
0.46	—	0.44	0.46	−0.02
0.46	0.30	0.70	0.76	−0.06
0.46	0.40	0.82	0.86	−0.04

The experimental error for the determination of zinc did not exceed ± 10%.

Determination of Zinc in Tap Water*

To 10 ml of test water contained in a platinum basin was added 0.5 ml of sulfuric acid sp. gr. 1.84. The solution was carefully evaporated until fumes of sulfur trioxide had ceased to be evolved. 0.25 ml of 1.0 N HCl, 9.75 ml of twice-distilled water, and 0.03 g of ascorbic acid or 0.2 g of hydroquinone for reducing any

* V. Babushkin and V. Lopatina, students at the Perm Medical Institute, took part in the determination of zinc in tap and spring water.

iron present, were added to the dry residue obtained by evaporation.

The contents of the platinum dish were mixed and filtered through a dry filter (treated with twice-distilled water beforehand). To 5 ml of this filtrate, 9 ml of the zinc reagent was added, and the liquid mixed by pouring from one tube into another; the final mixture was allowed to stand for 15 minutes and the zinc determined nephelometrically.

TABLE 6

Determination of Zinc in Tap Water

Tap water source	Zn found, mg/liter	Zn added, mg/liter	Total Zn found, mg/liter	Theor. Zn content, mg	Expt. error, mg
Factory A	0.24	—	0.24	—	—
	0.24	0.25	0.55	0.49	+0.06
Factory B	0.22	—	0.22	—	—
	0.22	0.25	0.48	0.47	+0.01
Factory C	0.35	—	0.35	—	—
	0.35	0.25	0.55	0.60	—0.05
Factory D	0.66	—	0.66	—	—
	0.66	0.25	0.90	0.91	—0.01

When the water contained organic material, 10 ml of the water was placed in a quartz Kjeldhal flask, and 1 ml of sulfuric acid sp. gr. 1.84 and 1 ml of hydrogen peroxide added. The mineralizate was transferred to a platinum dish and the flask rinsed out a few times with twice-distilled water; the solution was then evaporated to remove excess sulfuric acid. The procedure followed subsequently is the same as that outlined above. The experimental results are given in Table 6.

Determination of Zinc in Spring Water

Since the test drinking water (particularly the spring water) contained such small amounts of zinc, 200-250 ml of water was taken for analysis instead of 10 ml. The water was evaporated in a platinum dish and the procedure outlined above for tap water then followed.

TABLE 7

Determination of Zinc in Spring Water

Place of sampling	Zinc found, μg/liter
Spring No. 1, Egoshikh	10.0
No. 2	8.4
No. 3	8.5
No. 4	12.2
No. 5	12.5
Staryi Polskii village	100.0

The results obtained are given in Table 7.

SUMMARY

1. A new compound $[C_{24}H_{22}O_2N_4H]_2$ $[Zn(SCN)_4]$ has been prepared by the interaction of zinc with diantipyrylmethylmethane and thiocyanate in acid media.

2. Group I and II cations, aluminum, and manganese in amounts of 100 μg, trivalent iron in amounts

of 10 μg, and copper in amounts of 1 μg per ml of solution, do not interfere with determination of zinc in the form of the above compound by a nephelometric method.

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Received April 2, 1956

A NEW METHOD FOR THE FLUORIMETRIC DETERMINATION OF GALLIUM

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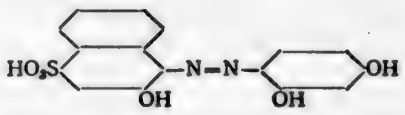
Several reagents have been suggested in the literature for the fluorimetric determination of gallium; they include: 8-hydroxquinoline [1-3], 5,7-dibromohydroxyquinoline [4], morine, and cupferron [5], salicylidene – ortho-aminophenol [6], and dyes of the solochrome group – solochrome red ERS, and solochrome black WDFA [7]. Solochrome group dyes, for example solochrome 6BFA [8,9], have also been described earlier as fluorescent indicators for the qualitative detection of gallium.

The methods described have a fairly low sensitivity (the limit of identification is 0.1 γ of gallium), and some of them, i.e. the most widely used one 8-hydroxyquinoline, are severly hampered by iron, separation of traces of which is not always easy and convenient.

In a search for a more specific and sensitive method of determining submicrogram amounts of gallium, we tried out a number of reagents suggested for this element by Poluektov and Kiseleva [10]. The most sensitive of them proved to be a dye – also of the solochrome group – 1,3-dihydroxybenzene - <4-azo-1> -2'-naphthol-4'-sulfonic acid (henceforth called sulfonaphthol-azoresorcinol), obtained by coupling diazotized 1-amino-2-naphthol-4-sulfonic acid with resorcinol.



This reagent, in an aqueous-alcohol solution at pH 3, gives in ultraviolet light a bright orange luminescence with gallium. By adding to 1 ml of a gallium solution containing 0.2 ml of 0.2 N hydrochloric acid, 0.2 ml of a chloride-acetate buffer (ph 3.0), 2 ml of 95% alcohol purified by distillation, and 0.2 ml of a 0.01% alcoholic solution of reagent, it is possible to detect as little as 0.01 γ of gallium on the basis of the weak orange-red luminescence when comparison is made with a blank. A series of solutions prepared in this way, and containing: 0.00–0.02–0.05–0.10–0.15–0.20–0.25–0.30–0.40–0.50 γ of gallium, form a well-defined standard scale, in which the intensity of the luminescence is proportional to increasing gallium concentration. The specificity of this reaction is better than that with 8-hydroxyquinoline. Table 1 contains data on the permissible amount amounts of certain elements in the test solution.

When using sulfonaphtholazoresorcinol for the quantitative determination of gallium in various natural materials, large amounts of accompanying metals should be removed. In many cases one can resort to the usual method of removing gallium – extraction of this element as its trichloride with ether. Such a separation, however, may prove insufficient during the analysis of samples containing tin, antimony, large amounts of copper, and other heavy metals, since certain amounts of these elements will also be extracted and get into the final solution. Consequently, in the given instance, we used a double separation: first, the heavy metals were removed by cementation on metallic cadmium [1], during which, in addition, iron was reduced to the divalent state; then the gallium was removed by extraction from divalent iron, aluminum, titanium, etc.

TABLE 1

Permissible Amounts of Various Elements during Gallium Detection

Element	Permissible amount, in γ	Element	Permissible amount, in γ
Aluminum	2	Zinc	2
Iron (III)	2	Antimony (III)	8
Iron (II)	10	Tin (IV)	15
Indium	100 •	Germanium	200
Titanium	10 •	Arsenic	15
Molybdenum	2	Phosphorus	2000
Thallium (I)	500	Calcium	10 •
Vanadium	1 •	Magnesium	10 •

•Large amounts of these elements were not tested.

Table 2 contains results for the determination of gallium in synthetic mixtures of various salts. Determination was carried out as described later. It is clear from Table 2 that when this analytical procedure is adopted, completely satisfactory results are obtained.

During determination of the gallium content of bauxites, silicates, sulfide ores, and waste materials from nonferrous metals, etc. the following method of getting the test material into solution was used. Bauxites were fused with potassium pyrosulfate, and the melt dissolved in water and hydrochloric acid. Silicates were broken down first with hydrofluoric and sulfuric acids, and then fused with potassium pyrosulfate as in the case of bauxites. Sulfide ores and nonferrous waste were given an acid treatment. Subsequently, in all cases cementation of the heavy metals on cadmium was carried out, followed by extraction of gallium chloride with ether. After removal of the ether, gallium was determined by means of sulfonaphtholazoresorcinol. Table 3 contains the results obtained for determination of gallium in bauxites, silicates, and wastes from zinc production. Table 3 also contains results obtained during determination of gallium which had been added to the test material before its break down.

TABLE 2

Determination of Gallium in Synthetic Mixtures

Ga added, in γ	Added, in mg	Ga found in γ	Difference in γ
50	—	49	—1
50	Al—30. Fe—40	50	0
50	Al—30. Fe—40. Cu—25. Sb—2. Sn—2	46	—4
12	Al—30. Fe—40. Cu—25. Sb—2. Sn—2. Mo—1	11.5	—0.5
12	Al—30. Fe—40. Cu—25. Sb—2. Sn—2. Mo—1. Zn—30. Pb—40. As—5	11.4	—0.6

During determination of gallium in coal, combustion may lead to partial volatilization of gallium. Accordingly, we tried out the possibility of rapid ashing of coal which would exclude loss of gallium. Of the various methods which we tried, the one that gave the most reliable results was heating the test material with a mixture of calcium oxide and nitrate. Thanks to the high sensitivity of the fluorimetric method involving sulfonaphtholresorcinol, it was sufficient to take for analysis an aliquot of 0.5—1 g; this meant that ashing could be speeded up. Calcination with calcium oxide of the residue obtained after ashing the coal favors decomposition of the silicate part of the coal, and the conversion of all the ashed part of the coal into a form which is soluble in acid. After ashing and calcining, the residue was dissolved in hydrochloric acid and the interfering elements removed by cementation on cadmium; gallium was then extracted as its trichloride, as in the analysis of ores.

Table 3 contains the results obtained for gallium determination in two samples of coal. Here, as in the case of ore analysis, some samples were analyzed after addition of gallium to the sample of coal before the treatment described above.

The fluorimetric method described also proved suitable for the determination of gallium in certain metals,

TABLE 3

Determination of Gallium in Ores, Coal, and Wastes

Test material	Sample wt., in g	Ga added, in γ	Ga found, plus that added		Test material	Sample wt., in g	Ga added in γ	Ga found, plus that added	
			in γ	in %				in γ	in %
Bauxite	0.2	—	8.2	0.0041	Silicate plus sulfides (flotation tailings)	0.5	—	9.3	0.0019
	0.2	—	8.8	0.0044		0.5	—	10.0	0.0020
	0.3	—	12.5	0.0042		0.5	6	16.0	0.0032
	0.2	8	16.4	0.0082		0.5	12	22.5	0.0045
	0.2	10	18.6	0.0093	Copper-cadmium cake	0.2	—	2.0	0.0010
Zinc concentrate	0.5	—	2.5	0.0005		0.2	1	3.0	0.0015
	0.5	—	3.0	0.0006		0.2	3	5.0	0.0025
	0.5	2	4.5	0.0009	Zinc cake	0.1	—	3.0	0.0030
	0.5	2	5.0	0.0010		0.2	—	6.8	0.0034
Lead concentrate	1.0	—	0.6	0.00006		0.2	6	13.0	0.0065
	1.0	—	0.5	0.00005	Coal I	1.0	—	2.0	0.00020
	1.0	0.5	1.1	0.00011		1.0	—	1.7	0.00017
	1.0	6.0	6.7	0.00067		1.0	2	3.7	0.00037
Sulfide-silicate ore	0.5	—	8.3	0.0017		1.0	3	4.7	0.00047
	0.5	—	8.0	0.0016	Coal II	1.0	—	0.2	0.000020
	0.5	12	20.0	0.0040		1.0	0.4	0.56	0.000056

in particular, in aluminum, zinc, and lead. Aluminum can be dissolved in hydrochloric acid. Zinc can also be dissolved in hydrochloric acid.

In both instances, where it is necessary to dissolve metallic tailings, nitric acid must be added. Lead is dissolved in nitric acid which is subsequently removed by evaporation with hydrochloric acid. In order to remove nitric acid completely, the residue should be evaporated with hydrochloric and formic acids. The heavy metals are then removed by cementation on cadmium, while gallium is extracted with ether as for ore analysis. Table 4 contains the results obtained during the analysis of gallium in samples of aluminum, zinc, and lead.

TABLE 4

Determination of Gallium in Aluminum, Zinc, and Lead

Sample	Sample wt.	Ga added in γ	Ga found, plus that added	
			in γ	in %
Technical aluminum, powder	0.2	—	25	0.0125
	0.1	—	13	0.0130
Pure aluminum, Duzharden factory, Dusseldorf	0.1	—	0.05	0.00005
	0.2	—	0.12	0.00006
	0.1	0.2	0.24	0.00024
Pure granulated zinc, "arsenic free"	0.5	—	0	0
	0.5	2.5	2.5	0.00050
	0.5	5.0	4.8	0.00096
Pure granulated lead	0.5	—	0	0
	0.5	2.5	2.5	0.0005
	0.5	4.0	4.0	0.0008

Analytical Procedure

Reagents: 1. Diethyl ether, free from peroxides, equilibriated with 6 N hydrochloric acid. 2. Ethanol, 96% purified by distillation. 3. Hydrochloric acid, 6 N, saturated with ether. 4. Hydrochloric acid, 0.2 N,

obtained by dilution with twice-distilled water of concentrated acid, obtained in turn by saturation of twice-distilled water with gaseous hydrogen chloride. 5. Chloracetate buffer (pH 3.0). A mixture of equal volumes of 0.5 M monochloroacetic acid and ammonium monochloroacetate. 6. Titanium trichloride, 20% solution in 6 N hydrochloric acid. This can be prepared from powdered titanium metal. 7. Water – twice-distilled – prepared in a quartz distillation apparatus. The twice-distilled water was only used in the later stages of the analysis for dissolving the residue after evaporation of the ether extract, and for preparing reagent. 4. In all other cases, ordinary distilled water was used. 8. Sulfonaphtholazoresorcinol, 0.01% alcoholic solution. 9. Calcium nitrate, prepared by dissolving 50 g of the tetrahydrate in 100 ml solution.

Dissolving the Test Material

a) Bauxite: 0.2 g of material was fused in a Pt crucible with 4 g of potassium pyrosulfate; after cooling, the melt was dissolved in 15 ml of water and 15 ml of concentrated hydrochloric acid on heating.

b) Silicates: 0.1-0.3 g of silicate was broken down with 5-10 ml of hydrofluoric acid and 0.5 ml of concentrated sulfuric acid. After removal of H_2F_2 by evaporation, 4 g of potassium pyrosulfate was added to the residue, and the procedure given for bauxite subsequently followed. Micas were fired before grinding and decomposing.

c) Sulfide Ores and Nonferrous Wastes. 0.1-1.0 g of sample (depending on the amount of gallium expected) was heated in a 100-ml beaker covered with a watch glass, with 10 ml of concentrated hydrochloric acid until hydrogen sulfide had ceased to come off. Heating was then continued while nitric acid was added in 0.2-ml lots (total amount 0.6 to 3 ml) until the test sample had broken down completely. The watch glass was next removed and the contents evaporated to dryness with hydrochloric acid added in two 2-ml lots. Finally, the residue was evaporated with a third 2-ml lot of hydrochloric acid to which 0.5 ml of 85% formic acid was added. The residue was dissolved on heating in 20 ml of 3 N hydrochloric acid.

In the case of poor sulfide ores, or of samples with a high silicate content, the latter must also be broken down. In such cases the test was broken down first with nitric acid, and then with H_2F_2 and H_2SO_4; the procedure followed subsequently was the same as that described for silicate analysis.

d) Aluminum, Zinc, Lead: 0.1-0.3 g of aluminum, or 0.1-0.5 g of zinc was dissolved on heating in 3 N hydrochloric acid. After the metal had dissolved, 0.5 ml of concentrated nitric acid was added and the mixture evaporated to dryness. The residue was evaporated twice with hydrochloric acid, and then with hydrochloric plus formic acid as for sulfide analysis.

Lead (0.2-0.5 g) was dissolved in nitric acid, after which the solution was evaporated to dryness; the residue was then evaporated a few times with hydrochloric acid, and finally with hydrochloric plus formic acid. The residue obtained by evaporation was dissolved in 20 ml of 3 N hydrochloric acid.

e) Coal. 1-2 g of finely ground coal was mixed in a platinum basin with 0.5 g of calcium oxide and 5 ml of calcium nitrate solution. The mixture was evaporated to dryness and dried on a sand bath. It was then heated in a muffle furnace, first at 400-500° and then, after the main bulk of the coal had burnt off, at 800° until all the carbon particles had been removed. In order to speed up the process, the lumps of burning material were broken up with a rod. The residue left after combustion was transferred to a 100-ml beaker; there it was moistened with water, and dissolved in 10 ml of concentrated hydrochloric acid. The solution was evaporated to dryness and the residue dissolved in 20 ml of 3 N hydrochloric acid.

Isolation of Gallium. To the solution obtained by any one of the techniques described above, without filtering it, was added 0.5-2 g of cadmium metal in the form of spongy metal or fine turnings, and the whole mixed for 5-10 minutes until the iron had been reduced (the solution becomes colorless), and the heavy metals had been deposited. When the iron was not completely reduced, the mixture was warmed slightly and again agitated for a few minutes. Completeness of removal of the heavy metals was controlled by addition of fresh cadmium turnings – fresh turnings should not become covered with a dark film. The solution finally obtained was filtered through a cotton wool plug washed with 3 N hydrochloric acid, into a separating funnel washed out with 6 N hydrochloric acid. To this filtrate was added 0.2 ml of titanium trichloride and the whole left to stand for 1 minute; 13 ml of 12 N hydrochloric acid was then added, and the solution extracted three times with ether – twice with 15 ml of ether, and the third time with 10 ml – the funnel being shaken for 1 minute each time. The combined ether extracts contained in another separating funnel were washed twice with 3-ml

lo's of 6 N hydrochloric acid. The washed extracts were poured into a 50-ml beaker containing 0.5 ml of a 10% solution of sodium chloride, and the ether carefully evaporated off; the residue was finally evaporated to dryness on a water bath. The residue was moistened with 0.5 ml 0.2 N hydrochloric acid and transferred to a 25-ml standard flask.

Determination. To 1 ml of the solution obtained, contained in a colorimeter tube, was added 0.20 ml of 0.2 N hydrochloric acid, 0.20 ml of 10% hydroxylamine solution, 0.20 ml of chloracetate buffer, 20 ml alcohol, and 0.20 ml sulfonaphtholazoresorcinol, and the whole mixed. After one hour the fluorescence of the solution was compared with the fluorescence of a series of standards prepared at the same time; the test tubes were examined against a black background in the filtered light of a mercury-quartz tube.

The standard series prepared covered the range 0.00-0.40 γ of gallium at intervals of 0.05 γ. A blank should be carried out, all the experimental procedure given above being followed for the blank.

When the gallium content of the sample is low, the residue left after evaporation of the ether can be dissolved in 10 ml or less of water rather than in 25 ml. In such cases, in preparing the standard series one must take into account the sodium chloride and hydrochloric acid content of the aliquot part of the solution taken for the determination.

SUMMARY

It has been shown that it is possible to use a reaction with 1,3-dihydroxybenzene-<4-azo-1>-2-napthol-4-sulfonic acid for the quantitative fluorimetric determination of gallium. On the basic of this reaction, a method has been developed for the determination of gallium in ores, coal, metals, and waste products of the nonferrous metal industry. The sensitivity of the method is as high as n x 10^{-5}% of gallium.

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Received May 16, 1957.

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DETERMINATION OF ZIRCONIUM BY MEANS OF AMMONIUM BENZENE-SELENINATE AND AMMONIUM NAPHTHALENESELENINATE

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Organic precipitants can be successfully used as well as inorganic reagents such as sodium phosphate, potassium iodate, and selenious acid, for the quantitative determination of zirconium, and for its separation from other elements. The most widely used methods are those involving precipitation with cupferron [1], and phenylarsonic and propylarsonic acids [2-4]. In recent years other precipitants have also been recommended, for example, mindalic acid [5-7] and its halogen derivatives [8], phthalic acid [9, 10] etc. All the reagents listed precipitate a certain limited number of elements, and the number of such elements can be restricted by using masking agents. A drawback of the precipitants is the fact that the compounds formed do not always correspond to the strictly stoichiometric formula, while coprecipitation of other elements is sometimes observed. As a result, the search for new organic reagents for zirconium and hafnium continues. Recently [11] benzenesulfinic acid $C_6H_5-SO_2H$ was suggested for the precipitation of zirconium, and for its separation from a number of other elements.

We have synthesized a large number of organic reagents containing the group $-SeO_2H$, which form sparingly soluble compounds with a number of quadrivalent elements (Ti, Zr, Hf, Ce^{IV}), and also with Nb and Ta [12]. The ones studied in greatest detail were benzene- and naphthalene- seleninic acids (and their ammonium salts). The present article contains descriptions of methods for determining zirconium and separating it from other elements.

The reagents $C_6H_5-SeO_2NH_4$ and $C_{10}H_7-SeO_2NH_4$ in strongly acid solutions of zirconium salts, form white amorphous precipitates, which on calcining give pure zirconium dioxide.

The limiting dilution at which precipitation of zirconium by means of the first reagent occurs is 1:1,000,000, while for the second reagent this limit is at 1:1,500,000.

The composition of the precipitates dried in air, according to analytical results approximates to the formula $ZrO(R\text{-}SeO_2)_2$; nevertheless, these compounds are not suitable for gravimetric use, accordingly, for the quantitative determination of zirconium, the precipitates are calcined and the residue of ZrO_2 weighed.

The variation in the composition of these compounds, as the variation in composition of a number of other compounds, is related to the tendency of zirconium salts, even in acid solution, to hydrolyze and also to form polymeric ions [13, 14].

In order to establish the optimum conditions for precipitating zirconium, we studied the effect of the concentration of various mineral acids. For this purpose, various amounts of nitric, hydrochloric, or sulfuric acids were added to a standard nitric acid solution of zirconium; the liquids were then diluted with water to 100 ml, and heated to the boiling point; precipitation of zirconium was effected by either ammonium benzeneseleninate or naphthaleneseleninate.

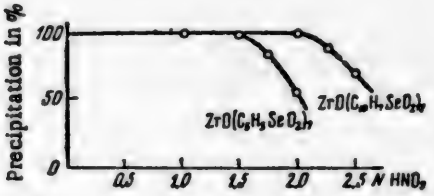
The solution plus precipitate was heated for 25-30 minutes, after which some macerated paper was added and, on cooling, the precipitate was filtered through a fine filter; the precipitate was washed with 0.1 N hydrochloric acid containing 0.4% of reagent, it was finally dried, and then calcined in a porcelain crucible at 800-900°.

On the basis of the results obtained (Fig. 1) the following optimum conditions for precipitation of zirconium were established:

Concentration of nitric or hydrochloric acid	1.0 N
Concentration of ammonium benezeneseleninate	0.7%
Concentration of ammonium naphthaleneseleninate	0.5%

For quantitative precipitation of zirconium from sulfuric acid solutions, a higher concentration of precipitant is necessary, since in this case formation of complex anions of $[ZrO(SO_4)_2]^{2-}$ occurs.

Determination of Zirconium by means of Ammonium Benzene- and Naphthaleneseleninate in the Presence of Aluminum, Beryllium, the Rare Earths, and Trivalent Iron. Since aluminum, beryllium, and the rare earths are not precipitated by ammonium benzene- or naphthaleneseleninate, it was decided to check experimentally on the possibility of carrying out a quantitative determination of zirconium in the presence of the elements indicated. Trivalent iron is precipitated by ammonium benzene- or naphthaleneseleninate; nevertheless, in contrast to that of zirconium, the precipitate given by iron is readily soluble in mineral acids.



Effect of HNO_3 concentration on precipitation of zirconium as the benzene- and naphthaleneseleninates.

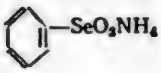
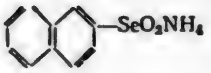
Results for the determination of zirconium in the presence of aluminum, beryllium, the rare earths, and trivalent iron are given in Table 1.

In the presence of large amounts of aluminum, beryllium, the rare earths, and iron, the precipitate is always contaminated by these elements; accordingly it is necessary to reprecipitate it.

Determination of Zirconium in the Presence of Titanium, Niobium, and Tantalum. Most elements are not precipitated in acid media by ammonium benzene- or naphthaleneseleninate and do not interfere with the determination of zirconium; exceptions are quadrivalent tin, titanium, niobium, and tantalum, which form similar precipitates in strongly acid solutions. Interference from the last three elements can be readily removed by addition of hydrogen peroxide, which forms complex compounds with these elements; hydrogen peroxide thereby prevents their precipitation, but does not affect the quantitative precipitation of zirconium. Tin should be removed beforehand by precipitation with hydrogen sulfide.

TABLE 1

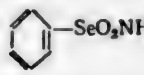
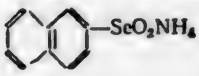
Determination of Zirconium in the Presence of Aluminum, Beryllium, the Rare Earths, and Trivalent Iron

Reagent	Taken, in mg					ZrO_2 found, in mg	Error, in mg
	Al_2O_3	BeO	Fe_2O_3	Σ r.e.	ZrO_2		
	250.0	—	—	—	1.22	1.23	+0.01
	250.0	—	—	—	1.22	1.22	±0.00
	—	300.0	—	—	1.22	1.20	−0.02
	—	300.0	—	—	1.22	1.19	−0.03
	—	—	30.0	—	1.22	1.25	+0.03
	—	—	30.0	—	1.22	1.24	+0.02
	—	—	—	150.0	1.22	1.19	−0.03
	—	—	—	150.0	1.22	1.24	+0.02
	250.0	—	—	—	1.22	1.20	−0.02
	250.0	—	—	—	1.22	1.21	−0.01
	—	—	30.0	—	1.22	1.24	+0.02
	—	—	30.0	—	1.22	1.22	±0.00
	—	—	—	150.0	1.22	1.25	+0.03
	—	—	—	150.0	1.22	1.25	+0.03

Precipitation of zirconium in the presence of hydrogen peroxide was carried out as follows. To the solution of the zirconium salt, 5 ml of 30% hydrogen peroxide was added, followed by 1.0 ml of 5-10 N hydrochloric acid,* the solution was then diluted with water to 100 ml and the zirconium precipitated with ammonium benzene- or naphthaleneseleninate.

TABLE 2

Determination of Zirconium by Precipitation with Ammonium Benzene- and Naphthaleneseleninate in the Presence of Hydrogen Peroxide

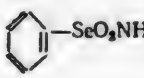
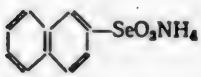
Reagent	ZrO_2 taken, in mg	ZrO_2 found, in mg	Error, in mg
	3.4	3.4	±0.0
	3.4	3.5	+0.1
	1.7	1.6	−0.1
	1.7	1.7	±0.0
	3.4	3.5	+0.1
	3.4	3.3	−0.1
	1.7	1.7	±0.0
	1.7	1.7	±0.0

For the determination of zirconium in the presence of titanium, niobium, and tantalum, the mixtures of oxides were fused with 10-12 times their amount of potassium pyrosulfate, and the melt dissolved in 3-5 ml of 30% hydrogen peroxide, 1-2 ml of sulfuric acid (1:1), and 40-50 ml water; the solution obtained was diluted with water to 100 ml and the zirconium precipitated with ammonium benzene- or naphthaleneseleninate.

The results obtained are given in Table 3.

TABLE 3

Determination of Zirconium in the Presence of Titanium, Niobium, and Tantalum

Reagent	Taken, in mg				ZrO_2 found, in mg	Error, in mg
	TiO_2	Nb_2O_5	Ta_2O_5	ZrO_2		
	17.0	—	—	1.7	1.6	−0.1
	17.0	—	—	1.7	1.8	+0.1
	—	14.0	—	1.7	1.7	±0.0
	—	14.0	—	1.7	1.6	−0.1
	—	—	12.0	1.7	1.8	+0.1
	—	—	12.0	1.7	1.6	−0.1
	17.0	—	—	1.7	1.8	−0.1
	17.0	—	—	1.7	1.6	−0.1
	—	14.0	—	1.7	1.8	+0.1
	—	14.0	—	1.7	1.7	±0.0
	—	—	12.0	1.7	1.6	−0.1
	—	—	12.0	1.7	1.8	+0.1

In the presence of large amounts of titanium, it is necessary, for its complete removal from zirconium, to reprecipitate the zirconium benzene- and naphthaleneseleninates; for this purpose the precipitate is washed with a small amount of water into the beaker in which the first precipitation was carried out and the precipitate

*In strongly acid solutions, hydrogen peroxide in the course of time partially reduces the reagents to $(RSe)_2$.

treated with 5 ml of concentrated HNO_3 with gentle warming; the liquid is then diluted with water to 100 ml and the zirconium reprecipitated.

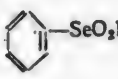
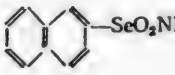
The completeness of the removal of zirconium from titanium was controlled by a photometric method involving hydrogen peroxide, while completeness of removal of zirconium from niobium and tantalum was controlled radiometrically, using the radioactive isotopes Zr^{95} and $Niobium^{95}$.

It was established that for a single precipitation of zirconium in the presence of titanium, niobium, and tantalum, in the quantities given in the table, less than 0.1 mg of the elements indicated could be found in the calcined residue of zirconium dioxide.

For objects with higher contents of niobium and tantalum, the benzene- and naphthaleneseleninate methods, like the phosphate and phenylarsonate methods, are unsuitable. In such cases, the precipitates of zirconium benzene- and naphthaleneseleninates contaminated with niobium and tantalum can, after calcination to give zirconium dioxide, be fused with potassium pyrosulfate, after which the melt is treated with 5% pyrogallic acid solution as described in [15]; the zirconium is then precipitated in the filtrate by means of ammonium benzene- or naphthaleneseleninate.

TABLE 4

Determination of Zirconium in Steel

Reagent	ZrO_2 added		ZrO_2 found		Error, in %
	in mg	in %	in mg	in %	
	3.59	1.44	3.59	1.44	±0.00
	3.59	1.44	3.60	1.44	±0.00
	7.18	2.88	7.17	2.88	±0.00
	7.18	2.88	7.20	2.89	+0.01
	3.59	1.44	3.58	1.44	±0.00
	3.59	1.44	3.56	1.43	—0.01
	7.18	2.88	7.16	2.87	—0.01
	7.18	2.88	7.21	2.89	+0.01

It should be pointed out that when precipitation of zirconium with ammonium benzene- or naphthaleneseleninate is carried out in the absence of hydrogen peroxide, the zirconium can be used as a collector for the isolation of small amounts of titanium, niobium, or tantalum. For this purpose a few milligrams of any zirconium salt is added to the test solution, and then precipitation effected with ammonium benzene- or naphthaleneseleninate; when such a procedure is followed, traces of titanium, niobium, and tantalum are coprecipitated with the zirconium. After filtration the precipitate is calcined and the residue fused with potassium pyrosulfate; titanium is then detected by the reaction with hydrogen peroxide, while niobium is detected as the thiocyanate [16], or niobium and tantalum are detected by means of pyrogallic acid [17].

Results for the determination of zirconium in steel and evdialite are given in Tables 4 and 5.

TABLE 5

Determination of Zirconium in Evdialite

ZrO_2 found, in %		
The phenylarsonate method	Benzeneseleninate method	The naphthaleneseleninate method
10.32	10.23	10.19
10.28	10.30	10.28
10.41	10.45	10.36

SUMMARY

Ammonium benzeneseleninate and ammonium naphthaleneseleninate are suggested as reagents for the determination of zirconium, and for its separation from a number of other elements (aluminum, beryllium, the rare earths, titanium, niobium, tantalum, and iron). These reagents in 1.0 N HCl give white precipitates with zirconium. The sensitivity of the reaction with the first

reagent is 1 : 1,000,000, while for the second it is 1 : 1,500,000. The composition of the precipitates obtained approximates to the formulas $ZrO(C_6H_5SeO_2)_2$ and $ZrO(C_{10}H_7SeO_2)_2$. For quantitative determinations these precipitates are calcined and the zirconium is weighed as ZrO_2. These reagents permit determination of zirconium in steel and eudialite. The absolute experimental error for zirconium contents ranging from 2.0 to 10% does not exceed $\pm$0.01%.

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Received May 23, 1957

*Original Russian pagination. See C.B. Translation.

AMPEROMETRIC TITRATION OF QUADRIVALENT URANIUM WITH AMMONIUM VANADATE

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The problem of the amperometric titration of uranium is one which has not been investigated enough. The discharge potentials of both quadrivalent and sexivalent uranium are known. The polarographic characteristics of the elements which can be used as oxidizing agents for the titration of quadrivalent uranium have been studied; a method has also been suggested for the amperometric titration of uranium with trivalent iron [1].

We used a solution of ammonium metavanadate as an oxidizing agent for the amperometric titration of quadrivalent uranium. Vanadium is reduced to the quadrivalent state on a dropping mercury electrode at a potential of about +0.1 volt.

The visual method for the vanadometric titration of quadrivalent uranium with phenylanthranilic acid, which was suggested by Syrokomskii [2] and which we have also studied, is very sensitive but its application is limited by the limits of the acidity of the solutions to be titrated of 5 N to 13.5 N with respect to sulfuric acid. When the acidity of the solution is less than 4 N and greater than 13.5 N, phenylanthranilic acid is unstable: in the first instance the color change is later, while in the second instance the color change is earlier than the equivalence point. Further, the visual method is not suitable for titration of colored solutions.

First of all, we took current – voltage curves for ammonium vanadate in the following media: 1 N H_2SO_4, 1 N HCl and 1 N $HClO_4$. It is clear from Fig. 1 that the limiting current for vanadium is clearly defined in all the acids indicated. By using these acids, it is possible to carry out amperometric determination of uranium in the potential range 0 to −0.16 volt.

TABLE 1

Potential 0 volt				Potential 0.1 volt			
U taken, in mg	V, ml NH_4NO_3 solution	U found, in mg	Error, in %	U, taken, in mg	V, ml NH_4NO_3 solution	U found, in mg	Error, in %
0.220	0.32	0.220	0	0.220	0.31	0.217	1.4
0.280	0.40	0.276	1.4	0.280	0.39	0.280	0

Titration of quadrivalent uranium was carried out at zero potential in sulfuric acid solution by means of 0.006 N ammonium vanadate. Hydrogen was passed through the system for 30 minutes prior to carrying out titration, in order to remove oxygen which interferes with titration. As an example we have given in Fig. 1 the curve obtained for 0.22 mg uranium (Fig. 2). Several determinations of uranium were carried out by means of the method described above at potentials of 0 and −0.1 volt.

It follows from the results given in Table 1 that amperometric titration of quadrivalent uranium by means of ammonium vanadate can be carried out with satisfactory accuracy, both at 0 volt, and at −0.1 volt.

In the following series of tests, uranium was titrated with ammonium vanadate in various acids. Changes in the acidity of the solution within the limits 0.1 N to 1 N, for sulfuric, hydrochloric, and perchloric acids have almost no effect on the titration results (Table 2).

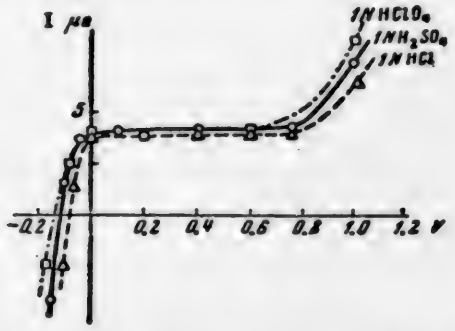

Fig. 1. Current – voltage curves for vanadium (5) in 1 N solutions of H_2SO_4, HCl, and $HClO_4$: O – 1 N H_2SO_4; Δ – 1 N HCl; □ – 1 N $HClO_4$.

Thus, uranium can be titrated with reasonable accuracy by means of 0.005 N ammonium metavanadate as long as the uranium concentration does not exceed 2.5 γ/ml; the mean relative error is 1-3%.

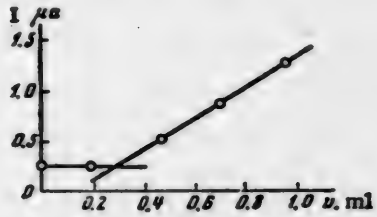

Fig. 2. Amperometric titration of quadrivalent uranium with 0.006 N ammonium vanadate solution.

Further dilution of the ammonium vanadate solution affects the shape of the curve considerably: the curve becomes flatter so that the error in determining the equivalence point increases.

The presence of the electrolytes: KCl, K_2SO_4, and NH_4Cl, for a solution with the same acidity in each case, namely H_2SO_4 (0.1 N), had no effect on the results of amperometric titration of uranium.

TABLE 2

(0.185 mg of U taken)

Acid	U found, in mg	Difference, in mg	Error, in %
0.1 *N* H_2SO_4	0.189	+0.004	2.2
1.0 *N* H_2SO_4	0.184	—0.001	0.6
0.1 *N* HCl	0.184	—0.001	0.6
1.0 *N* HCl	0.191	+0.006	3.2
0.1 *N* $HClO_4$	0.183	—0.002	1.1
1.0 *N* $HClO_4$	0.189	+0.004	2.2

TABLE 3

U taken in mg	Electrolyte content, in g	U found in mg	Difference, in mg
0.077	0.2 KCl	0.076	—0.001
0.094	2.0 KCl	0.092	—0.002
0.063	0.4 K_2SO_4	0.063	0
0.063	4.0 K_2SO_4	0.062	—0.001
0.063	1.3 NH_4Cl	0.061	—0.002

In view of the fact that iron is the element which accompanies uranium most often, it was of interest to find a method for determining uranium amperometrically without separating uranium from iron. In order to solve this problem, an attempt was made to complex iron as a stable complex ion.

A very good complexing agent for divalent iron is othophenanthroline ($C_{12}H_8N_2$), which complexes Fe^{2+} as a stable complex with a bright red color. Quinquevalent vanadium does not oxidize this complex compound. At the same time quadrivalent uranium does not form a complex with orthophenanthroline, and in the presence of the latter, uranium can be titrated completely with vanadate. In order to carry out determinations, the solution containing uranyl sulfate and iron sulfate (U : Fe = 1 : 25) was reduced with a liquid zinc amalgam in a hydrochloric acid solution, excess (10 mg) orthophenanthroline was then added; the solution thereupon acquired a bright red color; the volume of the solution was 25 ml while the H_2SO_4 concentration was 0.1 N. The results obtained are given in Table 4.

The mean error for the amperometric titration of uranium in the presence of iron complexed with orthophenanthroline amounts to 3-6%.

TABLE 4

U taken, in mg	U found in mg, in the presence of orthophenanthroline	U found, in mg, in presence of iron and orthophenanthroline	Difference in mg
0.091	0.090	0.093	+0.002
0.091	0.091	0.095	+0.004
0.120	—	0.122	+0.002
0.120	—	0.125	+0.005

TABLE 5

U taken, in mg	Complexon III, in mg	U found, in mg	Difference, in mg
0.258	25	0.259	+0.001
0.258	50	0.256	—0.002
0.162	100	0.168	+0.006
0.258	100	0.259	+0.001

TABLE 6

U taken, in mg	Element added		U found, mg	Error, in %
0.130	Cr	Weight ratio of M: U = 25: 1	0.135	3.9
0.190	Ni		0.196	3.1
0.162	Bi		0.156	3.7
0.192	Pb		0.189	1.6

For preventing possible hydrolysis, or formation of sparingly soluble sulfates, it is expedient to add Complexon III to the solution to complex lead, bismuth, chromium, and nickel. Addition of Complexon III does not affect the results of amperometric titration of uranium (Table 5).

Results of determinations of uranium in the presence of chromium, nickel, bismuth, and lead are given in Table 6.

SUMMARY

The possibility has been demonstrated of carrying out an amperometric titration of quadrivalent uranium (down to 2.5 γ/ml) by means of ammonium vanadate with an accuracy of 1-3%. Interference on the part of iron can be eliminated by addition of orthophenanthroline, while interference from chromium, nickel, lead, and bismuth can be eliminated by addition of Complexon III.

The mean error for uranium determination is 3-4%.

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Received February 8, 1957

CHROMATOGRAPHIC SEPARATION OF COBALT AND NICKEL DURING ANALYSIS OF ORES AND ALLOYS

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During the analysis of ores and alloys, cobalt and nickel, whose physicochemical properties are similar, are separated from each other by a number of chemical techniques; these techniques include precipitation of cobalt by α-nitroso-β-naphthol according to Ilinskii [1], Chugaev's method of separating nickel [1], precipitation of cobalt by persulfate and lead peroxide from sulfate solutions, and many others [2]. In addition to precipitation methods, extraction [3-5 etc] and electrolytic (in particular [6-8]) methods of separating these elements are also known.

Recently there have been indications that ion-exchange chromatography can be successfully used for this purpose; this technique has a number of advantages [9]; in particular, the anion-exchange method is being successfully developed. When metals are separated by the anion-exchange technique, the ones that are sorbed by the active groups of the resin are those that form complex anions.

Anion exchange frequently permits separation to be carried out in a shorter time than cation exchange. This cutting down of the time required for effecting separation is favored by the fact that desorption of complex anions sorbed by the anion-exchange resin from a medium containing a strong electrolyte, can be realized simply by changing the electrolyte concentration, or by using water.

In this connection, many different makes of anion-exchange resins have been synthesized recently. Several of them have found wide application, and have started to find use in analytical chemistry [10]. Of Russian anion-exchange resins, EDE-10 (a condensation product of ethylenediamine and epichlorohydrin) and AN-2F (the condensation product of polyethylenediamine, phenol, and formaldehyde) strongly recommend themselves. The most widely used foreign makes are the American resins Dowex-1, Dowex-2, and Amberlite IRA 400.

The problem which formed the subject of the work described here was to separate cobalt and nickel in a hydrochloric acid medium using EDE-10, and to develop a method which could be used for the analysis of ores and alloys. During a study of the sorption capacity of cobalt and nickel, results obtained previously on Dowex-1 were used [11]. It was found tha maximum absorption of cobalt occurs from 9 N HCl, in which it forms a fairly stable ion $[CoCl_4]^{2-}$, while nickel does not form appreciable concentrations of complex anions throughout the whole HCl concentration range (0.1—12 N).

The radioisotopes Co^{60} and Ni^{65} were used for studying the comparative sorption capacity of Dowex-1 and EDE-10. Their radiochemical purity was checked on the basis of their half-life periods and their maximum β-radiation energy. Columns 10 cm long and 5 mm in diameter were used. The particle size of the anion-exchange resins in the chloride form was about 50 mesh. Before loading the resin into the column it was washed with 9 N HCl; an active preparation of Co^{60} and Ni^{65} (20-30 thousand impulses/minute each) in 0.1-1 ml of concentrated HCl was then introduced onto the column. The column was eluted with 9 N HCl at the rate of 5-10 drops/minute. Nickel, which under these conditions does not form complex anions, passed into the filtrate. The filtrate was analyzed for nickel radiometrically; for this purpose 2 drops of filtrate was collected on a target; the solution was evaporated and the activity measured on a torsion counter. When all the nickel

had been eluted from the column, a fact which was established by the disappearance of activity in the filtrate, the cobalt was eluted with 0.5 N HCl. Under these conditions, the anion $[CoCl_4]^{2-}$ breaks down, and passes

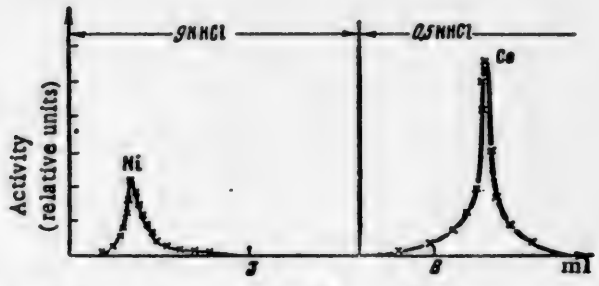

Fig. 1. Elution curves for Ni^{65} and Co^{60} on Dowex-1.

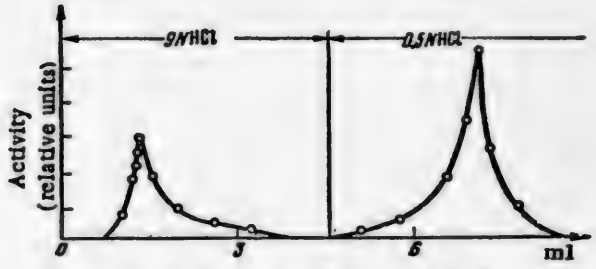

Fig. 2. Elution curves for Ni^{65} and Co^{60} on EDE-10.

into the filtrate in the form of its simple cation. This filtrate was also analyzed radiometrically. On the basis of these radiometric measurements, the elution curves for cobalt and nickel shown in Figs. 1 and 2 were constructed. These curves show that when the conditions outlined above are observed, complete separation of nickel and cobalt is achieved on both Dowex-1 and EDE-10. It is also evident that EDE-10 behaves like Dowex-1, although tailing is observed in the case of EDE-10; this tailing is probably the result of the fact that the EDE-10 resin was ground to give the requisite particle size, in contrast to Dowex-1 which is supplied in the form of small spheres; this grinding of the EDE-10 probably results in the formation of microcracks which slow down the elution process.

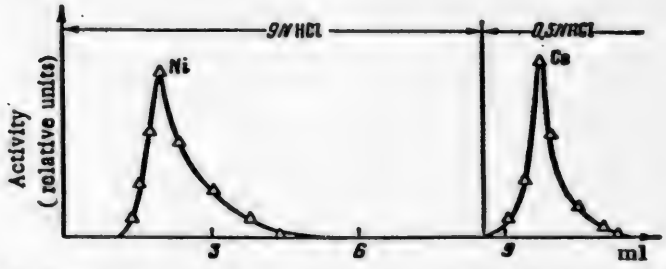

Fig. 3. Elution curves for weighable amounts of nickel and cobalt on EDE-10.

From the results of activity measurements carried out on the filtrates, the amount of cobalt and nickel separated from the columns was determined quantitatively by simply summing the activities. The results

obtained by this summation showed that cobalt and nickel are quantitatively eluted from the resin; no losses or mixing is observed.

Weighable amounts of cobalt and nickel were then separated on the same column using the same experimental technique as that described above. The analysis of the individual filtrates was carried out by means of color reactions in this case; nickel was detected with dimethylglyoxime, while cobalt was detected with α-nitroso-β-naphthol. During the elution process, the points at which nickel and cobalt started and finished passing into the filtrate respectively were established; elution curves (Fig. 3) were also constructed on the basis of visual observation of the changes in color intensity for the color reactions, and on the basis of radiometric control with added Co^{60} and Ni^{65}.

TABLE 1

Taken, in mg		Found, in mg		Difference, in mg		Error, in %	
Ni	Co	Ni	Co	Ni	Co	Ni	Co
0.503	3.5	0.498	3.41	—0.005	—0.009	—0.99	—2.55
0.503	3.5	0.496	3.5	—0.007	0	—1.4	0
1.06	1.75	1.10	1.78	+0.04	+0.03	+3.7	+1.71
1.06	1.75	1.07	1.79	+0.01	+0.04	+0.99	+2.28

Quantitative determination of cobalt and nickel in the appropriate fractions of the filtrate was realized by well-known gravimetric and photometric methods. Nickel was determined by the Chugaev method, while cobalt was determined by the Ilinskii method.

It follows from the results given in Table 1 that during separation of weighable amounts of cobalt and nickel, these elements quantitatively and separately pass into the corresponding fractions of the filtrate.

Determination of Cobalt and Nickel during the Analysis of Ores and Alloys. We had at our disposal an arsenic-cobalt ore containing S, Fe, Si, Ni and other impurities, and alloys containing about 20 elements including Fe, Co, Ni, Cr as base elements.

The methods of separating nickel with dimethylglyoxime and cobalt with α-nitroso-β-naphthol, particularly from solutions containing large amounts of components, are not suitable and are unreliable. Accordingly, on the one hand we made use of the similarity in physicochemical properties of cobalt and nickel when they are in a cationic state, for separating them from mixtures of other ions, while on the other hand the large difference in the capacity of the two elements to form complexes in hydrochloric acid solutions was used for separating these elements from each other. For isolating cobalt and nickel from solutions of ores and alloys, rubeanic acid was used, since this reagent selectively precipitates cobalt and nickel when copper is absent [12]. When

TABLE 2

Taken in imp./min			Found in prec. of rubeanates, imp./min			Precipitation, in %		
Fe	Co	Ni	Fe	Co	Ni	Fe	Co	Ni
6160	9216	2600	61	9200	2508	0.9	100.0	97.1
6160	9216	2600	42	9101	2475	0.7	98.8	96.9

copper is present, however, it still need not interfere with the final determination of cobalt and nickel, since it can be readily removed from them on the column on account of the comparatively high stability of its chloride complex in dilute HCl. In such a case, the cobalt is eluted with 4 N HCl, while the copper is eluted with 2.5 N HCl after the complete elution of cobalt. In order to check on the completeness of the separation of the rubeanates of cobalt and nickel by the technique described below, a synthetic mixture of cobalt and nickel to which Co^{58} and Ni^{65} had been added, was used. At the same time, the behavior of iron during precipitation of the rubeanates was established by means of the radioisotope Fe^{59}, since iron was a basic component of the ores and alloys at our disposal.

From the results given in Table 2, it is obvious that cobalt and nickel are completely precipitated by rubeanic acid, while iron – as the citrate complex – remains in the filtrate. Trapping of iron is reduced to a minimum by careful washing of the precipitate.

The ores were analyzed as follows. 500 mg of the ore was ignited in order to remove most of the sulfur and arsenic, after which the ore was dissolved in aqua regia. When decomposition was complete, the insoluble residue consisting of SiO_2 was filtered off. The residue was washed with dilute HCl and hot water. The filtrate plus washings were collected in a 25-ml standard flask and diluted to the mark with water. 2-4 ml aliquots of this solution were taken for analysis; to the aliquot was added 10% citric acid, after which the solution was neutralized with ammonia to a pH of about 8. 3-4 ml of a 0.5% solution of rubeanic acid was added to this solution. The precipitate obtained was left to stand for 3-4 hours, after which it was filtered through a No. 4 glass filter; it was washed 5-6 times with 1% NH_4Cl, and finally dissolved in aqua regia. The solution obtained, with a volume of 5-6 ml, was evaporated to dryness and the dry residue dissolved in the minimum volume of 9 N HCl. The subsequent analytical procedure adopted was that described above: the hydrochloric acid solution of cobalt and nickel was passed through a column of EDE-10 resin, after which the cobalt and nickel contents of the appropriate fractions of filtrate were determined by the usual analytical methods. The results obtained are given in Table 3.

TABLE 3

Sample	Sample weight, in mg	Found, in mg		Content in ore and alloys, %	
		Ni	Co	Ni	Co
Ore	20	0.3	4.249	1.51	20.1
	20	0.29	4.250	1.49	20.03
	40	0.59	8.55	1.50	20.20
Alloy*	40	5.054	4.18	12.62	10.42
	40	5.03	4.3	12.6	10.78

*Standard sample with a content of Ni –12.7%, Co –10.38%.

The alloy was analyzed as follows. 1 g of alloy was dissolved in aqua regia. When solution was complete, an aliquot of the solution was evaporated to dryness and the dry residue dissolved in HCl (sp.gr. 1.09) to which citric acid was added. The insoluble residue was filtered off and washed with dilute HCl, after which the filtrate plus washings were transferred to a 50-ml standard flask, and the volume made up to the mark with water. This solution was used for determining the nickel and cobalt content as described above.

It follows from the results given in Table 3 that the method of determining cobalt and nickel by means of an anion-exchange resin gives reasonably accurate results.

SUMMARY

Separation of weighable amounts of cobalt and nickel on an anion-exchange resin has been achieved by using conditions established beforehand by means of Co^{60} and Ni^{65}; the resin used was EDE-10. The method developed has been used for separating cobalt and nickel during analysis of ores and alloys.

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NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF NITROGEN, SULFUR, AND HALOGENS ON ONE ALIQUOT OF ORGANIC MATERIAL

COMMUNICATION 4. THE USE OF CALCIUM FOR DECOMPOSING TEST MATERIAL•

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In previous articles we have shown that nitrogen, sulfur, and halogens can be quantitatively determined in organic materials by means of powdered magnesium metal [1]. One of the drawbacks of the method is the necessity of treating the reaction mixture with acid, and this leads to the formation of an explosive mixture of silicon hydrides, hydrogen, and air; accordingly, the decomposition has to be carried out in an inert gas atmosphere. In order to simplify the magnesium method and to eleminate the drawbacks indicated, we decided to use powdered calcium instead of magnesium for determining nitrogen, sulfur, and halogens in organic materials.

Calcium, even at normal temperatures, reacts with water and readily combines with oxygen, nitrogen, sulfur, and halogens. The capacity of calcium, on heating, to combine with traces of air and other gaseous materials is used technically for creating a vacuum. Calcium in contrast to magnesium does not react with glass at 700-750°. The melting point of calcium is 850° while the boiling point is 1487°. Magnesium melts at 650° and boils at 1100°.

The method consists, in principle, of heating the test organic material containing nitrogen, sulfur, and halogens with powdered calcium at 700-750° in an atmosphere of ether vapor or hydrogen. Under these conditions calcium nitride, sulfide, and halides are formed and nitrogen, sulfur, and halogens are determined in these.

Determination of Nitrogen. The material was decomposed in the apparatus shown in Fig. 1.

The test material (0.0300-0.0600 g) was placed on the bottom of the glass tube 1 by means of a fine metal spatula.•• The aliquot was mixed with 20-30 mg of powdered calcium,••• and the mixture covered with a further 1-1.5 g of calcium. The layer of calcium in the tube should occupy 100-120 mm length of the tube. The air was displaced from the tube by pouring 1 ml of ether into it.

A rubber tube 2 connected to the tubes 3 and 4 was fitted onto the open end of the tube. A bunsen valve was fitted onto tube 3, and introduced under a cylinder containing water. The air in tubes 2,3 and 4 was also expelled by pouring 1.5 ml of ether into them. When tube 1 had been prepared for analysis, it was placed in a tubular open electric oven heated to 700-800°, or was heated with gas burners. First the layer of calcium furthest removed from the aliquot was heated; the heating zone was then gradually extended toward the aliquot. The heated calcium combined with all the gaseous products formed during the decomposition of the test material. This could be observed by sucking in of water and flattening of tube 1. In order to prevent

•Communication 3, J. Anal. Chem. 11, 233 (1956) (see C.B. Translation).

••The spatula was a fine copper wire 300 mm long, diameter 3 mm; one end was flattened to form a small blade suitable for introducing the test material into the tube.

•••Calcium should not be kept in contact with air for any length of time; it is best stored in glass bottles with ground glass stoppers, the bottles being filled with carbon dioxide.

water getting into the tube used for the analysis, tube 2 was fitted with a screw clip at the point where it was connected to tube 1. The screw clip was tightened up when the water being sucked into the apparatus appeared in the connecting glass tube 4.

When all the calcium layer had been heated to the temperatures indicated above (15-20 minutes) the electric oven was switched off. A vacuum should still be maintained in the cooled analytical tube (a point which could be verified by the fact that the rubber tube 2 was still flattened) otherwise the result for nitrogen would be too high. Decomposition of organic material by heating with calcium can also be carried out with another variant of the apparatus; this apparatus which is shown in Fig. 2 permits one to omit the stage of expelling the air by means of ether or hydrogen.

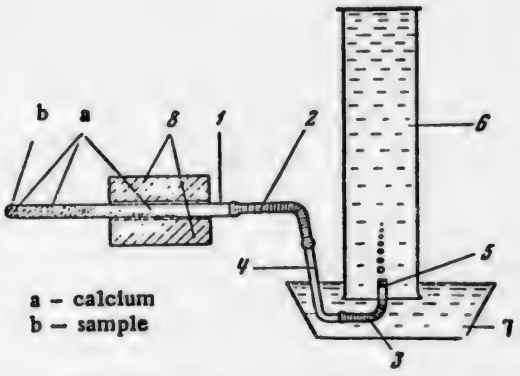

Fig. 1. Apparatus for decomposition of organic material: 1) glass tube 250 mm long with an internal diameter of 5-6 mm, fused at one end; 2 and 3) rubber tubing 200 mm long, 4-5 mm diameter; 4) glass tube; 5) Bunsen valve; 6) cylinder containing water; 7) crystallizing basin.

Tube 1 was prepared for analysis as described above and the aliquot of test material and powdered calcium introduced into it. In order to remove air from tube 1, 200-300 mg of powdered calcium was placed in quartz tube 3, and tubes 1 and 3 connected to each other by a piece of vacuum rubber tubing 2.

The calcium in tube 3 was heated first to 800°. The heated calcium in the course of 20 minutes combined with all the air in the apparatus. Tube 1 and its contents of test material was then heated as described above. When the tube had cooled it was withdrawn from the oven and cut open; the part of the tube not containing calcium was rejected, while the part of the tube containing test material and calcium was wrapped up in filter paper; the tube was then broken up in the filter paper by a few blows from a hammer and the whole transferred to a dry round-bottom flask for distilling off the ammonia. 20 ml of 0.05 N mineral acid and 2 drops of indicator (methyl red) were placed in the receiver. 80-100 ml of distilled water was introduced into the flask by means of a dropping funnel in order to decompose the reaction mass.• Since calcium reacts vigorously with water, the latter was added dropwise

Fig. 2. Simplified decomposition apparatus: 1) glass tube (described in the text); 2) rubber vacuum tubing 50-60 mm long; 3) quartz or porcelain tube 150 mm long, 6-7 mm in diameter fused at one end; a) calcium; b) test material.

initially. When the reaction had ceased the rest of the water was added. The flask was heated and the ammonia distilled over into the receiver (20-25 minutes). Excess acid in the receiver was titrated with 0.05 N alkali.

The results of some of these determinations are given in the Table.

Determination of Sulfur. Test material was decomposed in the apparatus shown in Fig. 1, the method used for determining nitrogen being followed. An aliquot of test material was introduced into tube 1 and

•Decomposition can also be effected with 30% ethanol. In this case the reaction is not quite so turbulent.

covered with 1-1.5 g of powdered calcium (see determination of nitrogen *).

Tube 1 was prepared for analysis and the apparatus assembled (Fig. 1).

Tube 1 was placed in the tubular open electric oven and heated as described for nitrogen determination. When heating was finished, the electric oven was switched off and the cooled tube withdrawn; the latter was then wrapped up in filter paper and broken up; the broken mixture of glass, paper and residue from decomposition were then transferred to a dry round-bottom distillation flask in order to drive off the hydrogen sulfide. Three absorption flasks were used for absorbing the hydrogen sulfide. The first of these contained 25-30 ml of a mixture of a 10% solution of sodium acetate and 10% zinc sulfate acidified with a few drops of concentrated acetic acid. The second and third flasks contained 20 and 10 ml respectively of the same mixture. A small excess of 4% sulfuric or hydrochloric acid was then added slowly — particularly to start with — to the distillation flask until the calcium had dissolved completely and the calcium sulfide had decomposed. When all the acid had been added the flask was heated and the hydrogen sulfide driven over with the hydrogen liberated. Distillation was stopped when one third of the contents of the flask had been distilled. The hydrogen sulfide was mainly absorbed as zinc sulfide in the first receiver.

When distillation was complete, the contents of all three receivers were poured together and 20 ml of 0.05 N iodine solution acidified with a few drops of 10% hydrochloric acid added; after standing for three minutes excess iodine was titrated with sodium thiosulfate. Results of some of these determinations are given in the Table.

Halogen Determination. The analysis was carried out in the apparatus shown in Fig. 1. The aliquot of test material and 1-1.5 g of powdered calcium were introduced into the tube 1 as described above (see determination of nitrogen) but, in contrast to the nitrogen determination, there was no need to expel the air from the flask.

Tube 1 was heated in the electric oven or with gas burners as described above. When heating had been completed, the cold tube was wrapped up in filter paper, the whole broken up with a hammer, and all the pieces transferred to a dry 0.5-liter tall beaker. The contents of the beaker were treated with 10-70 ml of 5% nitric acid, which was initially added dropwise in order to prevent sputtering of the solution. Acid was added until all the calcium had dissolved. The solid residue (carbon, glass) was filtered off and the filter plus solid residue washed carefully with distilled water. 20 ml of 0.05 N silver nitrate was added to the filtrate, and the solution titrated with 0.05 N ammonium thiocyanate in the presence of 0.5 ml of a saturated solution of ferric alum.**

Results of some determinations carried out in this way are given in the Table.

Determination of Sulfur and Nitrogen in Organic Materials on One Aliquot of Test Material. The aliquot of test material plus 1-1.5 g of calcium was placed in glass tube 1 of the apparatus shown in Figs. 1 and 2 (see nitrogen determination). The air was removed from the tube either by means of ether or by heating with calcium as described in the nitrogen determination.

Tube 1 prepared for analysis as described was then heated by the technique given above. When heating was finished, the tube was wrapped up in a filter paper, the whole broken up, and all the pieces transferred to the flask of the apparatus used for removing hydrogen sulfide (see sulfur determination). The reaction mass was decomposed with 80-100 ml of 4% sulfuric or hydrochloric acid, the hydrogen sulfide was distilled over and the sulfur content determined iodometrically (see sulfur determination). When the hydrogen sulfide had been determined, the condenser and the Kjeldhal setup was washed with distilled water, and the receivers for absorbing hydrogen sulfide replaced by a receiver for the ammonia (see nitrogen determination). The residue in the distillation flask was made alkaline with 50% alkali and, having distilled over the ammonia, the nitrogen determined.

Results of some of these determinations are given in the Table.

Determination of Nitrogen and Halogens on One Aliquot. Filling of the tube, expulsion of air from the

* When sulfur is determined there is no need to expel the air.

** Since commercial calcium metal always containssomechloride, it is essential to carry out a blank and correct for this chloride.

TABLE

Test material	Calc. N, %	Found N, %	Difference, %	Calc. S, %	Found, S, %	Difference, %	% Halogen calc.	% Halogen found	% Halogen difference
Para-aminobenzoic acid $C_7H_7O_2N$	10.21	10.13	—0.08						
Azobenzene $C_{12}H_{10}N_2$	15.37	15.36	—0.01						
α-Naphthylamine $C_{10}H_9N$	9.78	9.80	+0.02						
Diphenylamine $C_{12}H_{11}N$	8.27	8.29	+0.02						
Nitrocinnamic acid $C_9H_7O_4N$	7.25	7.01	—0.24						
Dimethylaminobenzene $C_{14}H_{15}N_3$	18.66	18.68	+0.02						
Acridine $C_{13}H_9N$	7.81	7.68	—0.13						
Sulfosalicylic acid $C_7H_{10}O_8S$				12.61	12.51	—0.10			
Meta-xylyltaurine $C_{10}H_{15}O_3NS$				13.98	13.81	—0.17			
Sodium 3-methyl-5-(α-furyl)-pyrazoline-1-dithiocarbonate $C_9H_9ON_2S_2Na$				25.82	25.78	—0.04			
Hexachloroethane C_2Cl_6							89.89	89.87	—0.02
Dibromobenzene $C_6H_4Br_2$							67.70	67.53	—0.17
1-Phenyl-3-carbethoxy-4-chloro-5-hydroxybenzofuran $C_{17}H_{13}O_4Cl$							11.19	11.23	+0.04
1-Phenyl-3-carbethoxy-7-chloro-5-hydroxybenzofuran $C_{17}H_{13}O_4Cl$							11.19	10.94	—0.25
1-Chloro-2,3-dimethyl-4-phenyl-butene-2 $C_{12}H_{15}Cl$							18.21	18.34	+0.13
1-Chloro-4-(para-chlorophenyl)-butene-2 $C_{10}H_{10}Cl_2$							35.26	35.07	—0.19
Para-toluenesulfamide $C_7H_9O_2NS$	8.18	8.01	—0.17	18.72	18.56	—0.16			
Diphenylthiourea $C_{13}H_{12}N_2S$	12.27	12.08	—0.19	14.04	13.83	—0.21			
Mercaptobenzthiazole C_7H_5NS	8.35	8.26	—0.09	38.31	38.08	—0.23			
3,5-Diphenylpyrazoline-1-thiocarbanilide $C_{22}H_{19}N_3S$	11.76	11.49	—0.27	9.00	9.03	+0.03			
S-(β-cyanethyl)-5-(α-furan)-3-methylpyrazoline-1-dithiocarbonic acid $C_{12}H_{13}ON_3S_2$	15.04	15.32	—0.28	22.95	23.00	+0.05			
3-Methyl-5,5-pentamethylenepyrazoline-1-thiocarbanilide $C_{16}H_{21}N_3S$	14.62	14.44	+0.18	11.15	10.83	—0.32			
1,3-Dimethyl-5-(1-amino-2-sulfo) ethylbenzene $C_{10}H_{15}O_3NS$	6.11	6.36	+0.25	13.98	14.08	+0.10			
1-Phenyl-2-methyl-3-acetyl-5-(para-bromobenzoxy)-indole $C_{24}H_{18}O_3NBr$	3.12	3.14	+0.02				17.82	17.87	+0.05
1-Ethyl-2-methyl-3-carbethoxy-4,7-dichloro-5-methoxyindole $C_{15}H_{17}O_3NCl_2$	4.24	4.40	+0.16				21.47	21.19	—0.28
Chloraniline C_6H_6NCl									
Sulfosalicylic acid $C_7H_{10}O_8S$	5.75	5.63	—0.12	6.01	5.83	—0.18	14.55	14.79	+0.24

apparatus, and heating of tube 1 were carried out according to the technique described already (see nitrogen and halogen determinations).

The reaction mass was transferred to the flask for distilling off the ammonia, where it was decomposed with water, the ammonia driven over and the nitrogen content determined (see nitrogen determination). When the ammonia had been driven off, the residue in the distillation flask was acidified with 5% nitric acid until the calcium hydroxide had dissolved completely; the solution was then filtered free of residual carbon and glass and the residue on the filter washed with distilled water; the halogen content of filtrate plus washings was then determined (see halogen determination).

Results of some of these determinations are given in the Table.

Determination of Sulfur and Halogens on One Aliquot. Analysis was carried out in the apparatus shown in Fig. 1. The reaction mass was transferred to a flask for driving off the hydrogen sulfide; there it was broken down with acid (see sulfur determination) and, having distilled over the hydrogen sulfide, the sulfur content determined iodometrically. The residue remaining after distilling off the hydrogen sulfide was filtered free of particles of carbon and glass. These particles were carefully washed on the filter with distilled water and the halogen content determined by the Volhard method as described already (see Halogen determination).

Results of some of these determinations are given in the Table.

Quantitative Determination of Nitrogen, Sulfur, and Halogens on One Aliquot of Organic Test Material. Decomposition of the organic material was carried out in the apparatus shown in Figs. 1 and 2. Introduction of test sample, filling the tube, and removing the air were carried out by the method described for nitrogen determination. When heating had been finished the cooled tube was broken up in a filter paper, and the pieces transferred to the flask of the apparatus used for distilling over the hydrogen sulfide; the reaction mass was decomposed in this flask with acid, and the hydrogen sulfide liberated distilled over into the receivers; the sulfur content of the original organic test material was then determined iodometrically, (see sulfur determination). In order to determine nitrogen the receivers used for absorbing hydrogen sulfide were replaced by a receiver for collecting ammonia (see simultaneous determination of sulfur and nitrogen). The acid solution in the distillation flask was made alkaline and the ammonia distilled over; the nitrogen content was then determined.

When both sulfur and nitrogen had been removed, the contents of the flask were acidified with nitric acid until all the calcium hydroxide had dissolved. Solid residues were filtered off, and washed on the filter with distilled water; the halogens were then determined argentometrically in the combined filtrate plus washings (see halogen determination).

Some results of determinations carried out in this way are given in the Table.

SUMMARY

A method is described for the quantitative determination of nitrogen, sulfur, and halogens in organic materials, in which the latter are heated with powdered calcium.

This method permits quantitative determination of the elements indicated either singly, in twos, or threes on one aliquot of test material. The use of calcium speeds up and simplifies analysis, and prevents formation of explosive mixtures.

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Received December 20, 1956

• Original Russian pagination. See C.B. Translation.

A MICRO METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS.

COMMUNICATION II.* DETERMINATION OF HALOGENS BY COMBUSTION IN A STREAM OF OXYGEN

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During determination of halogens in organic compounds it is essential to mineralize the halogens quantitatively, converting them thereby into the ionic state by oxidation or reduction. Of the reduction methods, we have studied that of Korshun and Chumachenko [1] – fusion of the organic material with potassium metal – while of the oxidation methods – the Pregl method [2] – we have tried breaking down the organic material by combustion in a stream of oxygen, and subsequently passing the gases over heated platinum and isolation of the combustion products of the halogen. Combustion was carried out in a quartz beaker. The liquid used for absorbing chlorine and bromine was a saturated solution of sodium carbonate to which a few drops of a saturated solution of hydrazine sulfate was added (instead of bisulfite), while for iodine the solution used for absorbing it was a 5% solution of sodium hydroxide. Chlorine was determined gravimetrically while iodine was determined volumetrically by the Leipert method [3] – titration with sodium thiosulfate. Analysis was carried out in apparatus made in the Klinsk Glass Factory "Laborpribor."

Because of defects in the apparatus the results obtained were low. The absorption apparatus connected via ground joints to the quartz tube was not made of heat-resisting glass.

During analysis of iodine-containing materials at an oxygen throughput of 4-8 ml per minute, some of the iodine was held back on the cold parts of the combustion tube and on the joints of the absorption apparatus. When the tube near the joints was heated in order to drive over all the iodine into the absorption apparatus, the joints cracked. The use of spirals in the absorption apparatus did not guarantee complete absorption of the gas by the absorption liquid, so that the results for chlorine and bromine were also low. Accordingly, in order to get better results, we used an apparatus similar to that recommended by Korshun and Sheveleva [4] for the simultaneous determination of carbon, hydrogen, and sulfur by a gravimetric method (Fig. 1).

The absorption apparatus which was connected to the combustion tube through ground joints was made from quartz; this made it possible to heat the tube near the joint and also heat the joint itself, and prevent deposition of iodine on the tube walls. In order to improve absorption efficiency, the absorption apparatus was half-filled with fine glass rings or beads. The combustion tube finished in a capillary nozzle, which passed into the absorption apparatus, and favored quantitative transfer of the gases into the absorption liquid.

In order to prevent possible breakthrough of gas, a test tube with a fused-in Schott disc was connected to the nozzle of the quartz absorption apparatus through a side capillary side tube, a piece of rubber tubing being used for connecting the capillary to the absorption apparatus. A hydraulic liquid seal of absorption liquid was set up in the test tube; part of the liquid being on the disc. The oxygen throughput was assessed by connecting the test tube to a Mariott bottle.

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*Communication I appears in J. Anal. Chem. 11, 728 (1956) (See C.B. Translation).

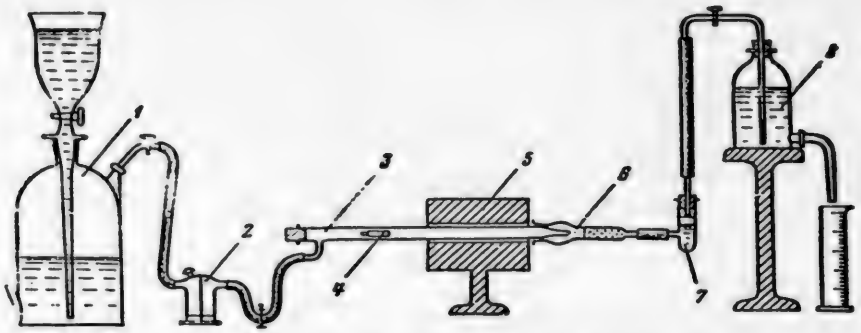
The results obtained on this setup, as can be seen from Table 1 are very close to the theoretical values.

TABLE 1

Test compound	Sample wt., mg	Halogen found, %	Halogen calc., %	Difference, %
Meta-iodobenzoic acid	3.210	51.05	51.39	—0.34
$I\text{-}C_6H_4COOH$	3.005	51.08		—0.31
β-Iodopropionic acid	4.580	63.39	63.46	—0.07
$I\text{-}CH_2CH_2COOH$	3.205	63.21		—0.25
Tetrachlorophthalic acid	4.435	46.85	46.70	+0.18
$C_6Cl_4(COOH)_2$	3.410	46.76		+0.16
α,α,2,3,4-pentachlorotoluene	5.510	67.03	67.10	—0.07
$C_6H_2Cl_3CHCl_2$	3.960	66.85		—0.25
α,α,α,2,3,4-hexachlorotoluene	3.100	71.27	71.24	+0.03
$C_6H_2Cl_3CCl_3$	4.350	71.37		+0.13

The Pregl method which is difficult and takes rather a long time, requires a platinum catalyst; chlorine and bromine are given a gravimetric finish. We were attracted by the simple and rapid macro-method of determining halogens proposed by Fedoseev and Sobko [5]. Combustion in this case again was carried out in a stream of oxygen, but the oxygen throughput was considerably greater, and no catalyst was used.

Potassium iodide was used as the absorption medium. The chlorine and bromine liberated during combustion of the organic material displaced a corresponding amount of iodine; iodine was trapped by potassium iodide. Sodium thiosulfate was used for titration. The apparatus described above was also used for this method of determining halogens.



1) Gasometer containing oxygen; 2) Tishchenko flask; 3) quartz tube, 8-9 mm inner diameter, 350-400 mm long; 4) quartz beaker containing test sample; 5) open electric oven 140 mm long, temperature 800-850°; 6) quartz absorption apparatus, connected via a ground joint to the combustion tube; 7) supplementary absorption apparatus with a side tube and porous disc; 8) Mariott flask.

Experimental Technique. 3-7 mg of test material was placed in a quartz tube, or in a quartz or platinum boat, and subjected to thermal decomposition by means of a gas burner or an electric oven at a temperature 950-1000°. The gaseous decomposition products mixed with the oxygen, the throughput of which was 20-25 ml/minute, and passed through a tube heated by an electric oven to 800-850°. The liberated halogen was trapped in the absorption apparatus by means of potassium iodide. The tube or boat containing the aliquot was placed at a distance of 40-50 mm from the oven. The aliquot was heated for 12-15 minutes; the amount of oxygen used during this period was 300 ml. The oven was then moved off, the gases driven out and the system allowed to cool for 8-10 minutes while another 200 ml of oxygen was used. The total amount of oxygen used was 500 ml.

During the analysis of high molecular weight materials, a larger volume of oxygen was used, amounting to 700-800 ml. Before commencing an analysis 1.0-1.5 ml of a 10% solution of potassium iodide was introduced into the quartz absorption apparatus which was connected to the test tube with the side tube; this solution of potassium iodide was carefully swirled round to moisten the glass rings or beads. Crystalline potassium iodide (0.5-0.7 g) was carefully strewn onto the porous disc and over the rings in the quartz apparatus by means of a funnel, without taking off the ground joint; the absorption apparatus was then connected to the combustion tube while the oxygen stream was kept on. When the tube or boat plus test sample had been introduced into the apparatus, heating was commenced, the burner being gradually brought closer to the neck of the tube or boat containing the sample, and the sample carefully ignited; it was finally completely burnt. When the substance had been completely burnt, the tube was heated along all its length up to the point where it joined the electric oven which was fitted right up to the joint of the absorption apparatus.

When the system was cooled the contents of the absorption apparatus was washed out with a few portions of distilled water into a conical flask; three washings were enough (7, 9, and 11 ml).

According to the observations of P. N. Fedoseev and M. Ia. Sobko, during combustion of chlorine-containing compounds, free chlorine and hydrogen chloride are formed. Accordingly, for determining the latter in the presence of chlorine, 9 ml of 0.02 N potassium iodate or potassium biiodate was added. In the latter case, it was essential to carry out a blank in order to take account of the free iodine liberated by potassium biiodate.* For bromine and iodine determinations, addition of potassium iodate or biiodate was not necessary, since during combustion of organic compounds containing bromine and iodine, only the free halogen is liberated. The amount of iodine was determined by titration with sodium thiosulfate.

TABLE 2

Test material	Sample wt., mg	Halogen found, %	Halogen calc., %	Difference, %
Poly para chloromethylstyrene $(C_8H_7CH_2Cl)_n$	3.360	23.50	23.30	+0.20
	3.650	23.43		+0.13
Sample IVS No. 8 $C_8H_{11}O_2Cl$	3.625	23.79	23.55	+0.42
	5.175	23.50		−0.05
Para-chloroaniline $C_6H_4ClNH_2$	3.325	28.28	27.95	+0.33
	3.375	28.31		+0.36
α-Chloroacrylic acid amide $CH_2=C(Cl)-CO_2NH_2$	3.610	33.96	33.60	+0.36
				+0.20
	4.090	33.80	33.60	−0.05
Tetrachlorophthalic acid $C_6Cl_4(COOH)_2$	4.185	46.65		+0.13
	3.345	46.83	46.70	+0.17
2, 4, 5-Trichlorotoluene $C_6H_2Cl_3(CH_3)$	4.850	54.64		−0.19
	3.100	54.28	54.47	−0.31
Polychlorovinyl $(-CH_2-CHCl-)_x$	3.115	56.42		−0.50
	3.305	56.23	56.73	−0.10
α, α, 2, 4, 5-Pentachlorotoluene $C_6H_2Cl_3 \cdot CHCl_2$	5.030	67.00	67.10	−0.49
	5.995	66.61		−0.58
Hexachloroethane C_2Cl_6	4.390	89.27	89.85	+0.11
Sample IVS No. 4 $C_8H_{15}Br$	6.830	41.95	41.84	+0.18
	3.390	42.02		+0.05
5, 7-Dibromo-8-hydroxyquinoline $Br_2C_9H_4(OH)N$	3.330	52.80	52.75	+0.09
	3.715	52.84		−0.01
Para-dibromobenzene $C_6H_4Br_2$	4.750	67.87	67.88	−0.18
	4.800	67.70		−0.05
	5.380	67.83		+0.19
Iodoalkylate of 1-methyl-2-(para-tolyl)-benzimidazole $C_{16}H_{17}IN_2$	3.790	35.04	34.85	+0.18
	4.410	35.03		−0.10
	3.860	51.29	51.39	0.23
Meta-iodobenzoic acid $I-C_6H_4-COOH$	3.700	51.16		+0.02
	3.620	51.41	63.46	+0.09
β-Iodopropionic acid $I-CH_2-CH_2-COOH$	4.350	63.55	63.46	+0.04
	3.280	63.50		

*Both potassium iodate and potassium biiodate can be used.

Before starting any analysis, 500 ml of oxygen was passed through the apparatus while the oven was switched on.

The analytical results are given in Table 2.

We successfully analyzed various halogenated polymers and copolymers, which are very difficult to analyze by combustion. Usually these compound only contain hydrogen, carbon, and oxygen in addition to the halogen. Analysis including sampling and titrating takes 35-40 minutes.

It should be pointed out that the micro method described above is not suitable for all organic materials. When the organic compound contains nitrogen as well as halogen, it is essential to know in what form it is present. Nitrogen present as amine, imine, or amide nitrogen or present in an aromatic nucleus does not interfere with halogen determination (Table 2). During pyrolysis of organic material in a quartz tube or boat, as Korshun and Limov observed [6, 7], nitrogen present in the forms indicated above is liberated in the elemental form. In nitro compounds part of the nitrogen is liberated as nitrogen oxides, and the results obtained will be high. In the same way it is impossible to analyze compounds containing sulfur as well as halogens; such compounds include free sulfonic acids and halosulfones.

The micro method developed was used for the determination of fluorine in organofluorine compounds. Analysis was carried out in the same apparatus. In contrast to the determination of the other halogens, the temperature of the oven was elevated to 950-1000° while a platinum contact was placed in the oven, or combustion was carried out in a platinum boat. During combustion the ground joint of the absorption apparatus was placed in the electric oven. Distilled water was used for absorbing the decomposition products.

When combustion was complete, the contents of the absorption apparatus was washed out into a conical flask. To this flask was added 0.5-0.7 g of crystalline potassium iodide and 9 ml of 0.02 N potassium iodate. The iodine liberated in an amount equivalent to the fluorine contained in the sample was titrated after 10 minutes with 0.02 N sodium thiosulfate.

TABLE 3

Test sample	Sample wt., mg	Halogen found in %	Halogen calc. in %	Difference, in %
Sample IVS No. 1	3.330	10.49	10.50	—0.01
	3.280	10.53		+0.03
Sample IVS No. 28	4.340	10.64	10.67	—0.03
	5.310	10.36		—0.31
Dimethylfluorostyrene $C_{10}H_{11}F$	3.190	12.61	12.66	+0.05
	3.550	12.62		+0.04
Methylfluorostyrene C_9H_9F	3.300	13.85	13.97	—0.12
	3.640	13.95		—0.02
	3.600	13.88		—0.09
Fluorobenzene C_6H_5F	3.400	19.87		+0.10
	3.380	19.77	19.77	0
	4.020	19.55		—0.22
1, 5-Hexafluoro-2-methyl-2-ol-pentanone-4 $CF_3 \cdot C(OH)(CH_3) \cdot CH_2 \cdot CO \cdot CF_3$	5.920	51.14	50.86	+0.28
	4.795	50.64		—0.22
Tetrafluoroethylene C_2F_4	3.345	76.04	76.00	+0.04
	4.150	72.26		+0.26

The results obtained are given in Table 3.

SUMMARY

On the basis of the macro method suggested by P. N. Fedoseev and M. Ia. Sobko, a micro method has been developed for the determination of bromine and iodine in organic compounds. It has been established that it is possible to use this micro method for the determination of fluorine in organic compounds, the com-

bustion products being absorbed with distilled water. The micro method developed can be used for both low molecular weight organic compounds, and for halogenated polymers which are difficult to burn.

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Received August 6, 1956

*In Russian.

**Original Russian pagination. See C.B. Translation.

POLAROGRAPHIC DETERMINATION OF FORMIC ACID

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The work described in the present article was devoted to a study of the polarographic behavior of formic acid, and to establishing whether or not the polarographic method can be used for determining formic acid and its salts in solution.

Measurements were carried out on a U-301 Heyrovsky recording polarograph with a mirror galvanometer. The sensitivity of the galvanometer without a shunt (S^0) was 4.44×10^{-9} amp/mm, at a distance of 0.9 meters. The dropping electrode and electrolyzer were of the type suggested by Heyrovsky [1]. The capillary characteristics were $m = 1.49$ mg/sec^{-1}; $t = 3.31$ sec; $m^{2/3} \cdot t^{1/6} = 1.592$ mg$^{2/3}$sec$^{-1/2}$. The anode was a mercury pool whose potential when measured with respect to the normal calomel electrode was found to be +0.060 volt.

Preliminary experiments showed that it is possible to get polarograms for formic acid in weakly acid solutions. The most suitable supporting electrolyte was found to be 0.1 N sodium or potassium chloride acidified with hydrochloric acid. Reduction of formic acid starts at 1.7-1.8 volts (relative to the normal calomel electrode); large maximum peaks were obtained on the polarogram in the region of the limiting current. Since these maxima were very difficult to suppress it may be supposed that this has been the reason for the fact that the polarographic behavior of formic acid has not hitherto been studied.

Ideas developed by one of the authors of this article [2] regarding the role of the null discharge potential in irreversible electrochemical processes, and the scale of φ-potentials • suggested on the basis of these ideas, enabled us to cut down the number of substances among which it is necessary to seek for additives to suppress the polarographic maxima.

The nature of the additives adsorbed on the electrode surface depends on the value of the φ-potential. Preferential adsorption will be shown by: in the case $\varphi < 0$, additives of a cationic type; in the case of $\varphi > 0$ additives of an anionic type, and in the case of $\varphi = 0$, additives of the molecular type. Under the conditions used for studying the polarographic behavior of formic acid $\varphi < 0$.•• Consequently, in order to suppress maxima in this particular case, one should look for additives of the cationic type.

Of the many cationic surface-active materials we tested the most suitable proved to be tribenzylamine — $(C_6H_5CH_2)_3N$. Tribenzylamine can suppress the maxima completely when a few drops of a saturated solution of this compound is added to 10 ml of a solution containing not more than 0.1 g mole/liter of formic acid; under these conditions, the pH of the test solution should be of the order of 2-4.

It is essential to point out that for each value of the pH of the solution, there is a permissible maximum concentration of formic acid for which it is still possible to get normal polarograms. Thus at pH 4 and pH 2, according to Fig. 1, the limiting concentrations of formic acid are equal to approximately 0.1 g mole/liter and 0.02 g mole/liter, respectively. Increasing the formic acid concentration beyond its limiting value, and also the use of solutions with pH < 2, lead to nonreproducible results. Under these conditions a visible film

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• φ-Potentials denote the shift in the stationary potential of the null discharge of the electrode metal.

•• According to the latest results, the potential for the null discharge of mercury is equal to −0.19 volt [3].

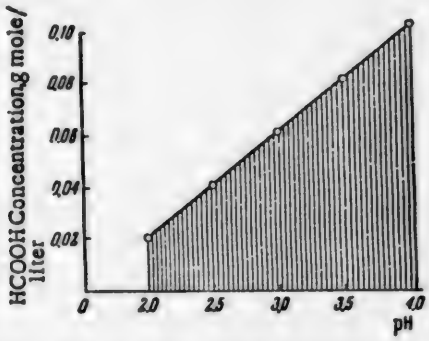

Fig. 1. Relation between the permissible concentration of formic acid and the pH of the solution during polarographic reduction of formic acid.

is formed on the mercury pool. Increasing the pH of the solutions beyond 4 is undesirable since subsequently, in order to maintain the value of the limiting current at a sufficiently high level, it is necessary to use comparatively high concentrations of formic acid. Tribenzylamine ceases to suppress the maxima and it also becomes impossible to obtain normal polarograms.

The shaded part in Fig. 1 corresponds to the values of formic acid concentrations for which it is possible to get normal polarograms.

Typical polarograms for formic acid in the absence and in the presence of tribenzylamine are shown in Figs. 2-4. In Fig. 5 are shown polarograms for the reduction of hydrogen ions at various pH values of the solution.

Results of the polarographic investigations showed that reduction of hydrogen ions accompanies reduction of formic acid.

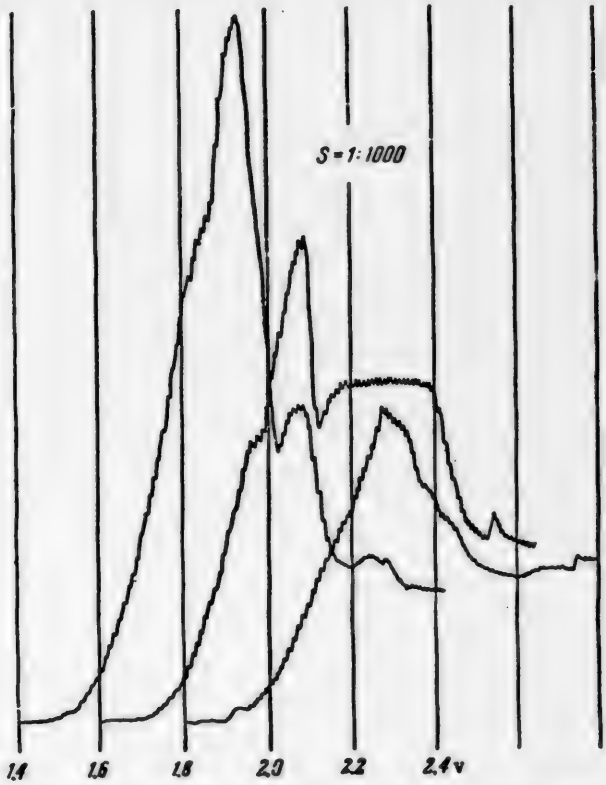

Fig. 2. Polarograms for formic acid in the absence of tribenzylamine.

The value of the limiting current increases on increasing the concentration of both the formic acid and the hydrogen ions. It is clear from Fig. 6 that with decreasing formic acid concentration the value of the

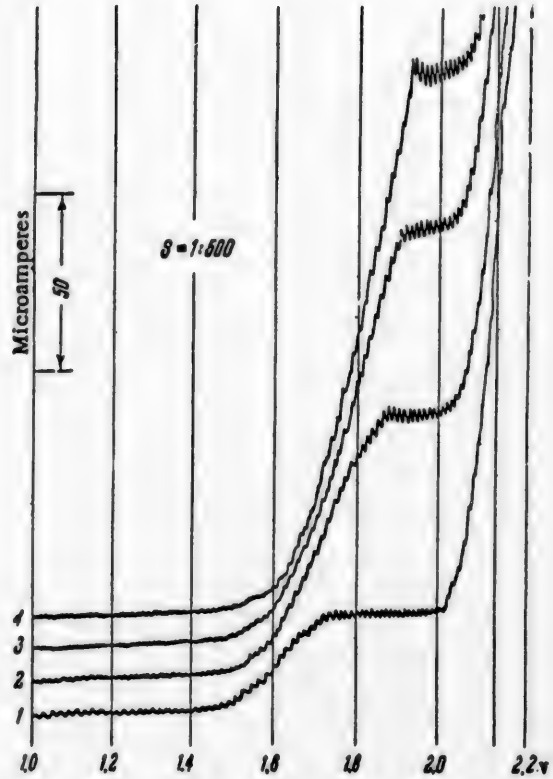

Fig. 3. Polarograms for formic acid at pH 2.46; 1) "Blank" (0.1 N NaCl); 2) 0.011 g mole/liter; 3) 0.022 g mole/liter; 4) 0.033 g mole/liter.

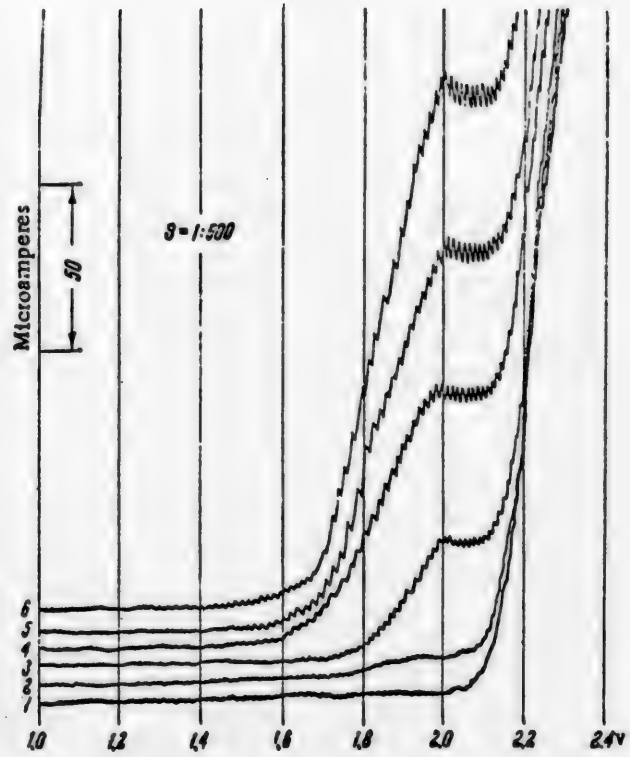

Fig. 4. Polarograms for formic acid at a constant concentration (0.11 g mole/liter) and at various pH values of the solutions; 1) pH 5.00; 2) pH 4.00; 3) pH 3.00; 4) pH 2.40; 5) pH 2.15; 6) pH 2.00.

total limiting currents approximates to the values of the limiting current for hydrogen at the given pH values of the solutions (Fig. 7). If the values corresponding only to the limiting currents of formic acid (excluding the limiting currents for hydrogen) are plotted along the ordinate instead of the value of the total limiting currents, then we get a linear relation between the concentration of the formic acid and its limiting current at various pH values of the solutions (Fig. 8).

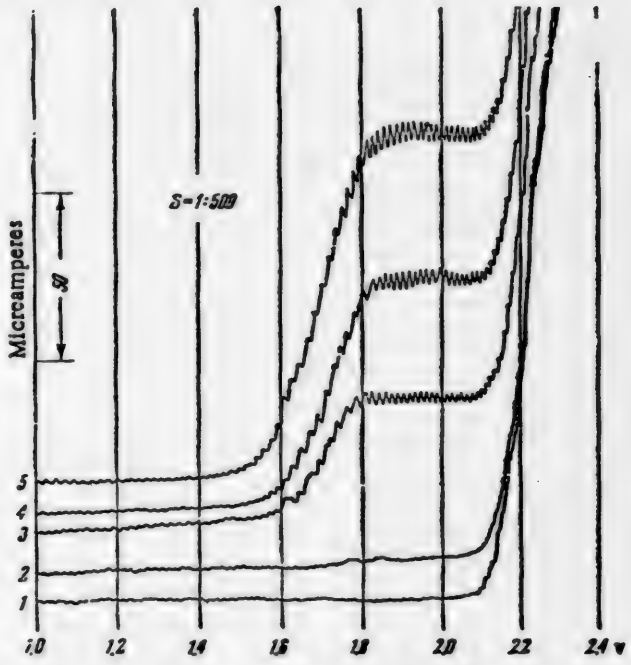

Fig. 5. Polarograms for hydrogen in 0.1 N NaCl acidified to various pH values by means of hydrochloric acid: 1) pH 4.00; 2) pH 3.00; 3) pH 2.40; 4) pH 2.15; 5) pH 2.00.

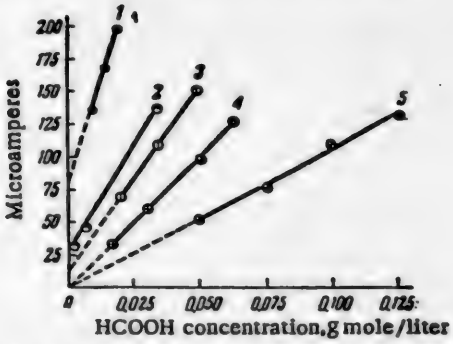

Fig. 6. Relation between the total limiting current and the concentration of formic acid at various pH values: 1) pH 2.00; 2) pH 2.46; 3) pH 3.00; 4) pH 3.50; 5) 4.00.

Thus the total limiting current is the sum of the limiting currents for the reduction of formic acid and of hydrogen ions. With increasing pH the limiting current which corresponds to reduction of hydrogen ions decreases, and starting at pH 3 and S = 1 : 500, is almost not recorded on the the polarograms. In Fig. 9, as an

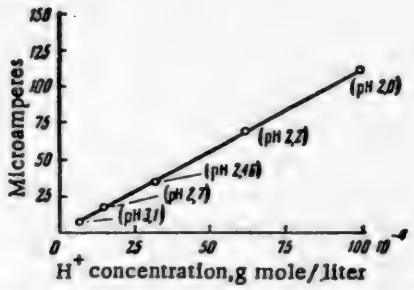

Fig. 7. Relation between hydrogen ion concentration and the limiting current.

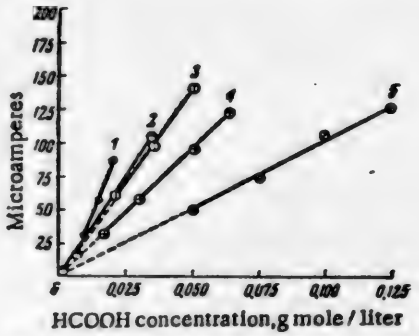

Fig. 8. Relation between formic acid concentration and the limiting current at various pH values of the solution: 1) pH 2.00; 2) pH 2.46; 3) pH 3.00; 4) pH 3.50; 5) pH 4.00.

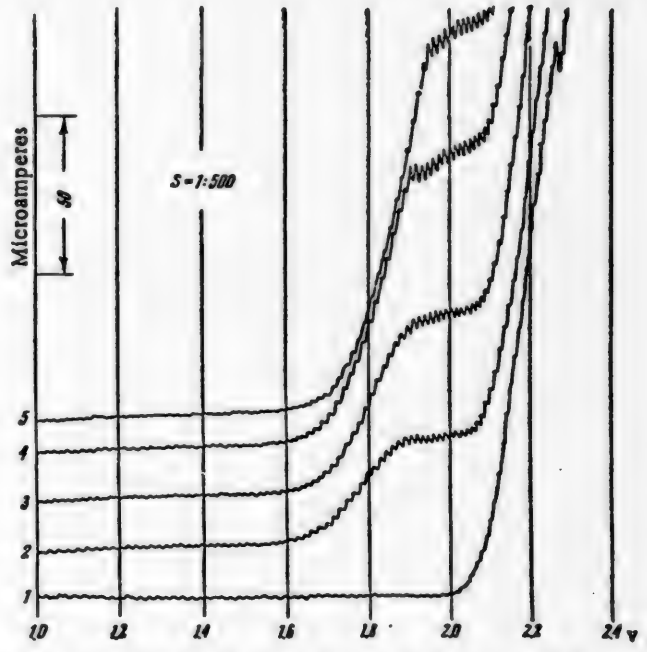

Fig. 9. Polarograms for formic acid at pH 3.5: 1) "Blank" solution (0.1 N NaCl); 2) 0.0165 g mole/liter; 3) 0.0302 g mole/liter; 4) 0.0505 g mole/liter; 5) 0.0640 g mole/liter.

example are shown polarograms taken at pH 3.5 and S = 1 : 500 for various formic acid concentrations. In this case it can be considered that the limiting current is almost completely determined by the formic acid concentration.

On the basis of what has been said above the following procedure is proposed for the polarographic determination of formic acid and its salts in solution.

An aliquot of test solution containing not more than 0.05-0.06 g mole/liter of formic acid is acidified to a definite pH value of 3-4; polarograms are then taken in a supporting electrolyte of 0.1 N sodium or potassium chloride, using a sensitivity of 1:500. A few drops (not more than 6) of a saturated solution of tribenzylamine is added per 10 ml of test solution to suppress the polarographic maxima. The addition or comparison techniques can be used for analysis. Whatever technique is used, polarograms of the standard solutions should be taken at the same pH values as those of the test solution. The presence of formaldehyde is not desirable, since the polarographic maxima which are characteristic of formic acid are not suppressed in this instance.

SUMMARY

In the presence of tribenzylamine, and under certain conditions, it is possible to get normal polarograms for formic acid. Optimum conditions have been established for the polarographic determination of formic acid and its salts in solution.

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A NEW METHOD FOR THE DETERMINATION OF MICRO AMOUNTS OF CITRIC ACID

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A number of photometric methods have been proposed for the determination of microgram amounts of citric acid. The most sensitive and specific of these methods are based on the color reactions of pentabromoacetone [1-5]. The latter is formed from citric acid during treatment of the latter with oxidizing agents (permanganate is the most often used) in mineral acid media and in the presence of bromine [6]:

$$HOOC \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH + O(KMnO_4) \rightarrow OC(CH_2 \cdot COOH)_2 + CO_2 + H_2O \quad (1)$$

acetone dicarboxylic acid

$$OC(CH_2COOH)_2 + 5Br_2 \rightarrow CBr_3 \cdot CO \cdot CHBr_2 + 2CO_2 + 5HBr \quad (2)$$

pentabromoacetone

We have established that pentabromoacetone is formed in high yield during electrolysis of citric acid on lead anodes using as anolyte sulfuric acid containing bromine ions.*

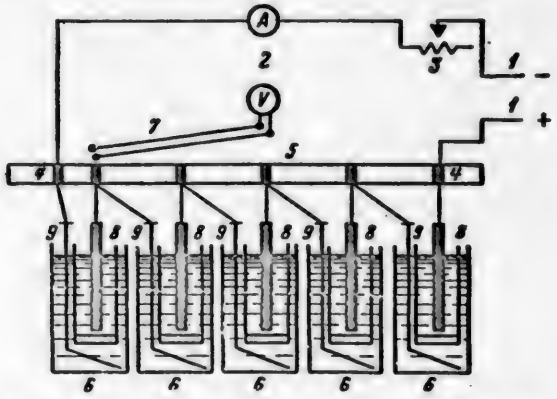


Fig. 1. Diagram of the apparatus: 1) Terminals connecting the apparatus to a dc source; 2) measuring apparatus; 3) rheostat; 4) plug socket for leading current to the terminals of the cathodes; 5) terminal junction for series connection of the five electrolytic cells (or parts of them); 6) electrolytic cell; 7) voltmeter contacts for connecting to the electrolytic cells; 8) anodes; 9) cathodes.

*Pentabromoacetone is not formed during electrolysis in acetic, phosphoric, or nitric acids. Under such conditions, the electrodes are not covered with lead dioxide, and the latter presumably is of significance for the electrosynthesis of pentabromoacetone.

A schematic diagram of the apparatus used for the electrolytic conversion of citric acid is shown in Fig. 1. A maximum and almost constant yield of pentabromoacetone is obtained for a certain value of the acidity of the electrolyte in the anode compartment (anolyte), for appropriate values of the current and voltage. Temperature changes from 20-40° do not appreciably affect the electrochemical process. The highest yield of pentabromoacetone is obtained in 2 N sulfuric acid containing 11 mg of potassium bromide, with a current of 0.2 amperes and a voltage of 3.0 volts. In this case the volume of the anolyte was 5 ml while the area of the working surface was 10.5 to 11.5 cm^2; this corresponded to an average current density of about 1.8 amperes/dm^2. Under these conditions, the duration of electrolysis was 45 minutes. The pentabromoacetone formed in the apparatus was determined by the highly sensitive Fujiwara reaction• (pyridine in a strongly alkaline medium [2, 7, 10, 18]).

Results of some special tests indicated that synthesis of the "dye" may proceed according to the following reactions:

$$CBr_3 \cdot CO \cdot CHBr_2 \xrightarrow{+NaOH} CHBr_3 + CHBr_2 \cdot COONa \qquad (3)$$

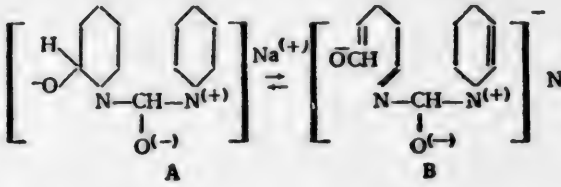
$$CHBr_3 + NaOH \rightarrow \rangle CBr_2 + NaBr + H_2O \qquad (4)$$

methylene bromide

$$\rangle CBr_2 + 2C_5H_5N \xrightarrow{+NaOH} \text{colored compound} \qquad (5)$$

(dye)

The most probable structure of the "dye" corresponds to the anion of the sodium salt (aci-salt) of the betaine of hydroxydihydropyridinemethinylpyridine (formula 6 A) or its tautomeric alicyclic form (formula 6B):



A B (6)

The cherry-red color which appears during the reaction for pentabromoacetone in the anolytes is partially masked by a yellow tinge which lowers the accuracy of photometric measurements. It has been found that this tinge is the result of the interaction of pyridine and persulfuric acid [8]; formation of the latter is catalyzed by bromine ions [9]. The effect of persulfuric acid can be completely eliminated by successive treatment of the reaction mixture after electrolysis with potassium bromide, sulfosalicylic acid, and potassium ferrocyanide. The intensity of the cherry-red color does not change as a result of this treatment.

The optical density of the solutions was measured on an "FM" photometer (with green filter S-53),•• while the turbidity of the solutions was eliminated by diluting them with an acetone-ammonia mixture; the color was stabilized by addition of a drop of concentrated alkali. Despite this, the optical density of the solutions still decreased gradually (mainly because of the effect of atmospheric carbon dioxide). Accordingly, photometric measurements were made not later than 15 minutes after formation of the colored compound, and during determination of a series of solutions the least colored solutions were measured first.

• No information has yet been published regarding the nature of the processes occurring during this reaction, nor has the composition of the cherry-red colored compound been established.

•• The "FEK" photocolorimeter is not quite so suitable, nor is the method of standard solutions.

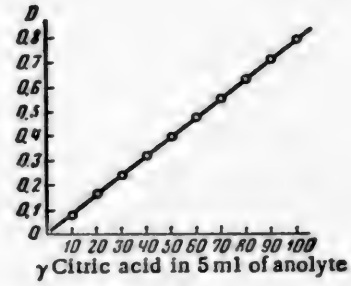


Fig. 2. Calibration curve.

During electrolysis of from 10 to 100 γ of citric acid, the optical density of the solutions obtained is proportional to the citric acid concentration of the anolyte (Fig. 2). Some of the acid presumably is oxidized further, since the optical density amounts to 80% of the values obtained with equivalent amounts of pure pentabromoacetone.

1. Construction of a Calibration Curve

Into the anode cells (Fig. 3) removed from the apparatus were measured 4-ml lots of standard solutions containing from 10 to 100 γ of citric acid. To these lots of standard solutions were added 0.5 ml of 20 N sulfuric acid, 0.4 ml of 0.33 N potassium bromide, and the volumes of the anolytes made up to 5 ml with distilled water. Lead electrodes • which had been mechanically cleaned to the polished metal surface were immersed in the anode cells, and the whole immersed in the catolyte – 1 N sulfuric acid. Catolyte and anolyte should be at the same level. The apparatus was connected to the dc supply and electrolysis carried out at 0.2 amperes and 3.0 volts.

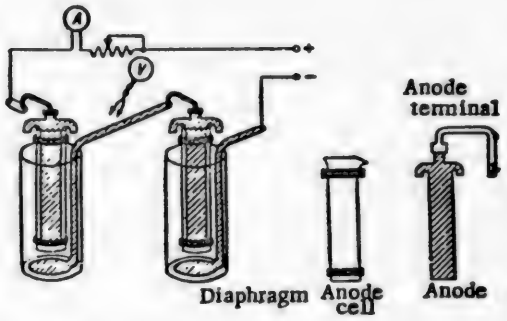


Fig. 3. Electrolytic cells (on the left) connected in series, and an anode cell (on the right) made of glass tubing (8 × 1.5 cm) with a cellophane diaphragm, fastened with a rubber ring; lead anode with terminal (11 × 0.13 × 0.2 cm).

TABLE 1

Determination of Citric Acid in Standard Solutions

Taken, in γ	Found (mean of five determinations), in γ
30.0	30.8
40.0	41.7
50.0	50.0
60.0	58.8
70.0	69.5
80.0	78.0
90.0	90.7
100	99.5

At the end of 45 minutes, the anode cells (together with the electrodes) were removed from the apparatus. Without removing the anodes, 0.5-ml lots of potassium bromide (24 g/100 ml) were added to the liquids. After standing for 5 minutes, the free bromine liberated was bound by means of 0.75 ml of 0.55 M sulfosalicylic acid. At the end of one minute, 0.1-ml lots of 0.48 N $K_4Fe(CN)_6$ solution were added to the completely colorless liquids. The slightly yellowish solutions were poured into 20-40-ml test tubes with ground glass stoppers.••

Each anode cell with its electrode was washed out with 3 ml of pyridine. The latter was then quantitatively combined with the main liquid, and 8 ml of sodium hydroxide solution (100 g NaOH in 150 ml water) added to each tube; the whole mixture in each tube was then thoroughly shaken for 20-30 seconds, and heated for 3 minutes in a bath at 80°. The heated tubes were all withdrawn simultaneously from the bath and cooled immediately in an ice bath. The pyridine layers acquired colors ranging from rose to cherry-red according to the

• Prepared from pure sheet lead.

•• In order to avoid loss it is advisable to use the anode for directing the stream of anolyte into the tubes.

citric acid concentration. In the control which did not contain citric acid, the color should only be a weak rose determined by trace impurities.

Measurements were carried out by transferring 2 ml of the colored, turbid pyridine layer into a 10-ml tube. A drop of 25% NaOH was added to this aliquot, followed by 5 ml of a mixture of acetone and concentrated ammonia (4:1). The mixed, and absolutely colorless solution was photometrically measured on an "FM" apparatus, using a 10-ml cell and a green S-53 filter. The reference solution was one composed of 2 ml of pure pyridine, 5 ml of the acetone-ammonia mixture, and a drop of alkali solution.

The method gives accurate and reproducible results (Table 1).

2. Determination of Citric Acid in Certain Biogenous Materials and in Medicinal Preparations

Using the method developed, citric acid was determined in a number of animal and plant materials, and also in medicinal preparations.

TABLE 2

Quantitative Determination of Citric Acid in Some Biogenous Materials and Medicinal Preparations

Test material	Citric acid found		Citric acid content according to literature, %
	our method	comparison method	
Potato (juice)	0.42 g/100 ml	0.40 g/100 ml••••	0.52 [10-13]
Bilberry (juice)	0.96%	0.89% •••••	0.91 [12]
Pomegranate (juice)	4.37 g/100 ml	4.18 g/100 ml•••••	5-9 [13, 14]
Lemon (juice)	6.26 g/100 ml	5.83 g/100 ml•••••	5-7 [13, 15]
Tomato	0.85%	0.65%•••••	0.61 [12, 13]
Mushrooms•	0.23%	0.20% ••••	0.35 [12]
Milk• (cow's)	0.14 g/100 ml	0.12 g/100 ml•••••	0.18-0.25 [13-16]
Bones• (horned cattle)	0.50%	0.44%•••••	Up to 1.6 on the dry weight
Saliva•	1.09 mg/100 ml	0.48 ml/100 ml•••••	0.1-5.0 mg/100 ml [13]
Citramon tablets••	3.1%	3.29%	~4
"Novomigrophen" tablets •••	2.98%	3.21%	~3

• Proteins were precipitated beforehand.

•• Contained citric acid, aspirin , phenacetin, caffeine, and cocoa.

••• Contained citric acid, phenacetin, caffeine, pyramidone, and starch.

•••• Taussky and Shorr method [17].

••••• Taylor's method [18].

Numerous components of the biosubstrate will be found in the plant and animal samples and, accordingly, in the anolyte. In separate experiments it was established that after electrolysis and the pyridine reaction, 100 γ of the following compounds did not give a color: arginine, ascorbic acid, acetone, alanine, acetylcholine-iodide, aspartic acid, allantoin, alloxane, acetaldehyde, glycine, glucosamine, guanidine, inositol, glycerophosphoric, glutamic, levulinic, maleic, lactic, uric, and nicotinic acids, urea, caffeine, xanthine, creatine, creatinine, pyruvic acid, hydrogen cyanide, pectin, thiamine, acetic acid, fructose, furfurol, formaldehyde, ethanol, and succinic acid.

The compounds listed below give a color equivalent to 10-40 γ citric acid: tyrosine, histidine, adrenaline, phenylpyruvic acid, butyric acid, phenol, quinic acid, hydroquinone, pyrocatechol, phenylalanine, tryptophane, crotonic acid. In addition, a color was observed in the case of acetoacetic, malonic, β-hydroxymalonic, and malic acids.

Despite the fact that some of the compounds listed above were found in the test natural objects, determination of citric acid was always selective (for results, see Table 2). This is partly explained by their removal during the procedure used (see below), and also by the considerably dilution.

Procedure for Determination of Citric Acid in Biogenous Substrates. The components of the biosubstrate in a number of objects did not lower the specificity of the determination. Aliquots of such objects in the form of extracts or juice were diluted with water until the citric acid concentration was 10-100 γ citric acid in 4 ml. The procedure followed subsequently was the same as that used for determination of citric acid in its pure aqueous solutions. In some cases more accurate results were obtained by precipitating proteins beforehand in aliquots of test material* (See Table 3).

Reference solutions used for the analysis were prepared as follows. Into a 20-30-ml test tube was measured out a volume of test solution equal to that introduced into the anolyte. To this test tube was added 1.0 ml of 10 N sulfuric acid, 0.1 ml of potassium bromide solution (24 g/100 ml), 0.1 ml of potassium bromate (0.5 g/100 ml), and the solution diluted to 5 ml with distilled water. The subsequent treatment of this solution was carried out simultaneously with the preparation of the anolytes for the color reaction after the anolytes had been electrolyzed.

TABLE 3

Preparation of Plant and Animal Material for Citric Acid Determination

Test material		Final dilution of extract or aliquot		Extract taken for determination, ml	
		without precipitation of proteins	after precipitation of proteins	without precipitation of proteins	after precipitation of proteins
Potato	Juice tested	1 : 100		2.0	
Bilberry		1 : 500		3.0	
Pomegranates		1 : 2000		2.0	
Lemons		1 : 2000		2.0	
Tomatoes	The sample was grounded up with water, and the extract filtered through a glass filter	1 : 4000		2.0	
Mushrooms	The sample was ground with water and left to stand for about one hour		1 : 16		0.25
Milk (cow's)	Whole milk was diluted with water in the ratio of 1 : 10		1 : 40		1.00
Bones (horned cattle)	The samples of dry, degreased bone flour was heated with 5% HBr		1 : 100		1.50
Saliva (human	The proteins were precipitated and the protein-free centrifugate evaporated to a volume equal to half of that of the sample of saliva originally taken				1.00

Note. The proteins were precipitated by adding a 10% solution of phosphotungstic acid to part of the sample until precipitate ceased to separate out. The precipitate was centrifuged. The clear centrifugate was diluted with water and an aliquot taken for analysis.

In contrast to the main solution, the reference solution usually remained colorless; sometimes, however, it had a rose color; the reference solution was used for the colorimetric measurements, the procedure outlined above for preparing the solutions for measurement being followed.

*Of the materials generally used for precipitating proteins, trichloroacetic acid should not be used, since this compound gives a color with pyridine and alkali.

Procedures for Determination of Citric Acid in Citramon and Novomigrophen Tablets. The ground tablets were extracted three times with 10-ml lots of benzene. The insoluble residue was kept at 90° until the solvent had been removed by evaporation, and was then quantitatively transferred to a 500-ml standard flask; 20 ml of 1 N sulfuric acid was then added and the solution made up to the mark with water. After the flask had been shaken and the turbidity allowed to settle, 2 ml of the solution was taken for determination, the same procedure as that outlined for determination of citric acid in its pure solutions being followed.

SUMMARY

A new method for the determination of 10-100 γ of citric acid has been developed, which is based on its conversion into pentabromoacetone on a lead anode, with a subsequent photocolorimetric determination based on the color formed by the interaction of pentabromoacetone with pyridine and alkali. The method permits a fairly rapid and selective determination of citric acid in various vegetables, berries, fruits, in bones, saliva, and milk, and also in medicinal preparations.

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Received December 24, 1956

PHOTONEPHELOMETRIC DETERMINATION OF VITAMIN B_1 (THIAMINE)

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A large number of methods have been developed for the quantitative determination of vitamin B_1 (thiamine) in pharmaceutical preparations and other materials [1-14]; all the same, many of these methods are not suitable for practical purposes. We have developed a rapid photonephelometric method which is based on the fact that thiamine is completely precipitated from solution at pH 4.5-5.5 by phosphotungstic acid. The method is applicable to the determination of thiamine in injection solutions, yeast, and some medicinal mixtures. The limit of identification for thiamine hydrochloride is 2 γ in 1 ml of reaction mixture.

The stock solution used was a 5% solution of crystalline thiamine hydrochloride.

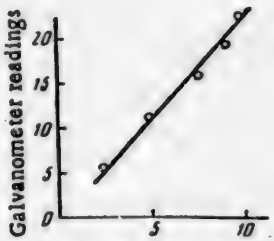
Nephelometric measurements were carried out on a V. E. Nize type photonephelometer, with a differential setup with two selenium photoelements and electrical compensation. The sensitivity of the mirror galvanometer was 1×10^{-8} amperes/division. Voltage variation in the circuit within the limits 80-150 volts was stabilized with a ferroresonance stabilizer having a power of 14 watts; the capacity of the cell was 35 ml.

After establishing the optimum conditions for precipitating thiamine and obtaining a turbidity suitable for quantitative measurements, the following method was developed.

The calibration curve was constructed as follows: known volumes of a 0.05% solution of thiamine hydrochloride (0.2, 0.5, 0.7, 1.0, 1.5 ml) were introduced by means of a micropipet into 50-ml flasks; water was then added to each flask in such amount as to leave room for the addition of 1 ml of 0.01 M sodium phosphotungstate and — if necessary — the volume made up accurately to the mark with water. The contents of the flasks were transferred to 100-ml conical flasks, the whole shaken up thoroughly and nephelometric measurements carried out. The readings obtained on the nephelometer after 5 minutes were then used for constructing a calibration curve. Not more than 30 minutes are usually required for constructing such a curve.

Thiamine hydrochloride was determined in 5% injection solutions as follows: 1 ml of test solution was diluted to the mark with distilled water in a 100-ml standard flask; 0.5 ml of this solution was transferred to a 50-ml standard flask, and distilled water added in such amount as to leave room for addition of 1 ml of 0.01 M sodium phosphotungstate; after the latter had been added, the volume was then made up to the mark with distilled water. The contents of the 50-ml flask were then transferred to a 100-ml conical flask where they were thoroughly shaken up and nephelometric measurements carried out.

Determination of the Thiamine Content of Yeast and Medicinal Mixtures. Since vitamins A, B_2, C, D, and PP, which enter into the composition of yeast, are not precipitated by sodium phosphotungstate, thiamine can be determined in this material as follows. The total weight of sample submitted for analysis was determined and a fifth of this amount taken. When the amount of sample available was less than 15 g, then the whole amount was taken for thiamine determination. Weighing was carried out on a technical-chemical balance. The mean weight of one sample of yeast taken from several dozens was determined. The material taken for analysis was ground up in a porcelain mortar until a homogeneous powder was obtained. Two lots of 5 g of this powder were weighed on an analytical balance, and each lot dissolved in distilled water in two 50-ml flasks. From each flask 12.5 ml was pipetted out into 50-ml standard flasks when the yeast contained about 2 mg of thiamine, while 25-ml lots were pipetted out when the thiamine content was 1 mg. The sub-



Calibration curve for thiamine determination.

sequent procedure followed was the same as that described for 5% injection solutions. Determination can also be carried out on one sample of yeast.

Of the various materials contained in medicinal preparations only pyramidone interferes with thiamine determination. In such cases a sample of the powder merely treated 3-4 times with 5-ml lots of chloroform on a filter paper contained in a funnel. The pyramidone passed into the filtrate. The thiamine remained on the funnel (the solubility of thiamine in chloroform is 1 : 200,000 [1]) together with ascorbic acid. The residue on the funnel was treated several times with water and the filtrates collected in a 100-ml standard flask; the volume was made up to the mark with water and the whole thoroughly mixed; 1 ml of this solution was transferred to a 50-ml standard flask and the procedure outlined above followed.

Preparation	Composition, in g	Thiamine found, in g	Error, in %
Yeast	Thiamine 0.00200 Sugar 0.024480	0.00194	3
Yeast	Thiamine 0.00100 Ascorbic acid 0.02500 Vitamin B_2 0.0010 Vitamin A 1650 Sugar	0.00095	5
Yeast	Thiamine 0.00100 Ascorbic acid 0.02500	0.00096	4
Injection solution	Thiamine 5%	4.9	2
Powder	Thiamine 0.00200 Nicotinic acid 0.02 Ascorbic acid 0.05 Glucose 0.5	0.00196	2
Powder	Thiamine 0.050 Ascorbic acid 0.1 Pyramidon 0.8	0.048	4

The results given in the Table show that the method developed permits determination of small amounts of thiamine in mixtures with reasonable accuracy.

SUMMARY

A method which has been developed for the determination of thiamine (Vitamin B_1) in preparations turned out by the vitamin industry, and in medicinal preparations, is based on precipitation of thiamine by sodium phosphotungstate. The experimental error does not exceed 5%. The limit of identification is 2.5 γ of thiamine hydrochloride in 1 ml of reaction mixture.

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Received October 22, 1956

A METHOD FOR THE QUANTITATIVE DETERMINATION OF DIMETHYLPHENYLCARBINOL

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Determination of tertiary alcohols by the usual esterification methods with acetic anhydride, phthalic anhydride, or acetyl chloride always leads to low results, since under the conditions used for esterification they are partially dehydrated. The general method of Mitchell and Smith [1] is also inapplicable, since in our case it was necessary to determine dimethylphenylcarbinol (DMPC) in mixtures with phenol and acetophenone, which, during acetylation in the presence of boron trifluoride, react with the water liberated. The method based on hydrochlorination of DMPC, followed by decomposition of the chloride with alkali, and determination of chloride ions with silver nitrate is exceedingly long. For the same reasons, under production conditions the method according to which DMPC is quantitatively dehydrated, while the α-methylstyrene formed is determined by means of mercuric acetate in methanolic solution, is also inapplicable.

In order to find an analytical method for the quantitative determination of DMPC which is reliable enough, and is readily carried out under production conditions, the work described here was undertaken. The method selected was based on two processes: a) dehydration of DMPC, and b) titration of the water liberated with Fischer reagent. Chief attention was given to developing the conditions for quantitative dehydration of DMPC.

In order to study the percentage dehydration of the carbinol under various conditions, an aliquot of catalyst (cupric sulfate, boron anhydride, sulfuric acid, and sodium bisulfate) was introduced into a 100-ml flask fitted with a ground glass stopper; this was followed by 10 ml of isopropylbenzene as solvent for DMPC, and an aliquot (0.1-0.3 g) of the test carbinol. The flask was connected to a reflux condenser and heated for 10-60 minutes. The condenser was then washed down with another 10 ml of isopropylbenzene, and the whole cooled to room temperature. Then, by means of a pipet and without disturbing the deposit of catalyst, a sample (10-15 ml) of the liquid in the flask was transferred to another similar flask and titrated with Fischer reagent. A blank was carried out in parallel using the same conditions and reagents but omitting the carbinol.

TABLE 1

Wt. of DMPC, g	Wt. of sodium bisulfate, g	DMPC determined, g	DMPC determined, %	Wt. of DMPC, g	Wt. of sodium bisulfate, g	DMPC determined, g	DMPC determined, %
0.920	0.1	0.898	97.7	0.0824	0.2	0.0824	100.0
0.1068	0.1	0.1003	94.0	0.1578	0.2	0.1571	99.6
0.1534	0.1	0.1489	97.0	0.1672	0.2	0.1666	99.7
0.1784	0.1	0.1717	96.2	0.1854	0.2	0.1872	101.0
0.0664	0.2	0.657	99.0	0.1882	0.2	0.1882	100.0

It was established that the maximum percentate dehydration of DMPC in the presence of cupric sulfate as catalyst did not exceed 28%, while it was 26% in the case of boric anhydride and sulfuric acid. The highest

percentage dehydration of 92% was achieved on adding 2 drops of concentrated sulfuric acid. When the concentrated acid was used, the mixture was only heated to 85° and was kept at this temperature for 15 minutes; at higher temperatures resinification occurred which interfered with titration.

Dehydration of DMPC in the presence of sodium bisulfate was appreciably better; no resinification was observed. This permitted the temperature to be increased almost to the boiling point of the isopropylbenzene. In order to avoid loss of water, the contents of the flask were not boiled but only brought up to incipient boiling (152°). The sample was kept at this temperature for 10 minutes.

As can be seen from Table 1, quantitative dehydration of DMPC was achieved on using 0.2 g of sodium bisulfate.

In order to study the effect of impurities on the accuracy of determination of DMPC, experiments were carried out on its dehydration in the presence of phenol, dimethylphenylparacresol, acetophenone, and α-methylstyrene; DMPC was determined initially in the presence of each of these compounds taken separately, and then in mixtures of these compounds. In all cases, 0.2 g of sodium bisulfate was added; heating was carried out at 152°, the sample being held at this temperature for 10 minutes.

TABLE 2

Weight of DMPC in g	Impurity		DMPC found, in g	DMPC determined as % of that taken
	Nature of impurity	Weight, in g		
0.1162	Phenol	0.2288	0.1162	100.0
	Acetophenone	0.3452		
	DMPPC	0.2140		
0.1284	Phenol	0.7332	0.1276	99.3
	Acetophenone	0.1060		
	DMPPC	0.2028		
0.1180	Phenol	3.3122	0.1168	99.0
	Acetophenone	0.4480		
	DMPPC	0.1712		
0.2276	Phenol	0.2768	0.2248	99.8
	Acetophenone	0.3570		
	DMPPC	0.1372		
	α-Methylstyrene	0.1868		
0.1218	Phenol	0.3020	0.1206	98.9
	DMPPC	0.2885		
	Acetophenone	0.2196		
	α-Methylstyrene	0.1989		

From the results given in Table 2 it is obvious that phenol, dimethylphenylparacresol (DMPPC), acetophenone, and α-methylstyrene, present as impurities, do not interfere with determination of DMPC.

SUMMARY

A method has been developed for the quantitative determination of dimethylphenylcarbinol in industrial mixtures. Phenol, dimethylphenylparacresol, acetophenone, and α-methylstyrene do not interfere.

The experimental error is about 1%. A single determination does not take more than 25 minutes.

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THE PHOTOMETRIC DETERMINATION OF ZINC

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Modern photoelectric apparatus guarantee such a high degree of accuracy for the measurement of light absorption that it is possible to carry out photometric determinations of large amounts of an element, for example up to 15% of zinc. We have developed an indirect method for determination of zinc which is based on its precipitation [1-4] as $(C_{13}H_{17}ON_3)_2 \cdot H_2[Zn(SCN)_4]$, with subsequent formation of molybdenum blue by partial reduction of phosphotungstomolybdic acid with pyramidon.

Pyramidon was determined colorimetrically by measuring out 2-10 ml of pyramidon solution (1.13 mg/ml) – corresponding to 0.1-0.5 mg of zinc oxide – into a 100-ml standard flask, and adding 70-80 ml of water, and 10 ml of phosphotungstomolybdic acid, and making up to the mark with water. The solutions to be poured together and the water were warmed to 20° beforehand. The solution obtained was then kept for 1.5 hours at 20°.

The phosphotungstomolybdic acid was prepared as follows [5]: 0.4 g of ammonium phosphomolybdate and 20 g of sodium tungstate were boiled for 2 hours with 10 ml of 87% phosphoric acid and 150 ml of water under reflux. On cooling, the solution was diluted with water to 200 ml and filtered.

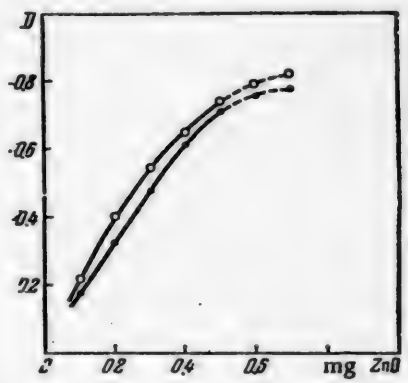

Fig. 1. Calibration curves for the photoelectric colorimeter FEK-M: O – By titration of pyramidon solution; ● – after precipitation of zinc from the solution to be titrated in the form of $(C_{13}H_{17}ON_3)_2 \cdot H_2[Zn(SCN)_4]$.

The optical density was measured after 1.5-3 hours in 20-mm cells using a red filter. Control cells were filled with water.

Zinc was precipitated by mixing the test solution, pyramidon and potassium thiocyanate in the presence of acetic acid [1-4]. The precipitate formed is readily soluble; the choice of a wash liquor presented difficulty. As our experiments showed, amyl acetate was suitable for this purpose.

The total volume of the solution during precipitation, duration of precipitation, and precipitation temperature are of importance for the quantitative precipitation of zinc.

A twelve-fold excess of sodium, potassium, magnesium, calcium, aluminium, and antimony, taken either separately or together, do not interfere with determination of 0.1 mg of zinc oxide. On increasing the amount of zinc oxide to 0.5 mg, the same cations do not interfere appreciably when present in amounts which are twice that of zinc. No tests were carried out with greater amounts of impurities. Barium, lead, and trivalent iron interfere with zinc determination; barium and lead are removed as the sulfates.

Before determination of zinc, the precipitant for zinc is prepared; for this purpose equal parts of a 4% solution of pyramidon and a 50% solution of potassium thiocyanate are mixed; to this mixture is added glacial

acetic acid on the basis of 0.3 ml acetic acid per 20 ml of mixture. 5 ml of test solution containing 0.1-0.5 mg of zinc oxide* is measured into a special beaker fitted with a nozzle and a ground glass stopper (e.g. 60-mm tall, 30-mm diameter), 2 ml of precipitant solution is then added and the whole mixed. The beaker is covered and kept in a thermostat for 2-3 hours at 30 ± 1°. The precipitate is then filtered off under vacuum and washed 5 times with amyl acetate, the latter being taken in 1-ml portions. The amyl acetate remaining is removed by heating the beaker on a boiling water bath.

The precipitated zinc salt is dissolved in hot water and transferred to a 100-ml standard flask, in which it is made up to 70-80 ml with water; the pyramidon is then determined as described above.

The calibration curves are shown in the figure.

The results obtained are always low. This, however, does not prevent determination of zinc with an accuracy of 0.1-0.3% (by weight).

For zinc contents greater than 0.5 mg in the test solution the method is not applicable. Good results were obtained for the determination of zinc in glass. (See Table).

Determination of Zinc in Glass

Zinc added, in terms of ZnO, %	ZnO found, %					Error, %
	Determinations				Mean	
	1	2	3	4		
0.93	1.06	1.10	—	—	1.08	+0.15
1.56	1.47	1.53	—	—	1.50	—0.06
5.05	4.88	5.08	4.95	5.05	4.98	—0.07
6.58	6.48	6.32	6.36	6.30	6.37	—0.21
10.25	10.24	10.16	10.28	10.32	10.25	0
14.96	14.85	15.15	—	—	15.00	+0.04

SUMMARY

A new photometric method has been developed for the determination of up to 15% of zinc (calculated as ZnO). Zinc is precipitated as zinc dipyramidotetrathiocyanate, and the pyramidon content of the latter determined by formation of molybdenum blue from phosphotungstomolybdic acid. The effect of other ions has been studied. One determination, without decomposition of the material, takes 4 hours.

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* 0.1-0.4 g of test material is taken depending on the expected zinc content. For silicates the amount of hydrofluoric acid used is 1-5 ml while the amount of nitric acid is 10-15 ml. If these amounts of zinc are contained in a smaller volume, then the latter is made up to 5 ml with water.

SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

COMMUNICATION 6. DETERMINATION OF CADMIUM, GERMANIUM, INDIUM, GALLIUM, GOLD, ANTIMONY, AND LEAD IN URANOUS-URANIC OXIDE*

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The principles of the evaporation method have been published previously [1-3], and the possibility has been demonstrated of determining B, Li, Mn and some other elements present as impurities in U_3O_8, Al_2O_3, ThO_2, and BeO which are of low volatility. The main condition which ensures the efficiency of the evaporation method is that there should be a large difference between the volatilities of the impurities to be determined and that of the main component. In order to increase the sensitivity of the determination, it is often necessary to modify the method of preparing the test sample (evaporation of impurity) and of carrying out the spectrographic analysis of the concentrates. The present article is devoted to the application of the evaporation method for determining a group of volatile elements (Cd, In, Ge, Ga, Au, Sb, and Pb) in uranous-uranic oxide. In the case under consideration, some difficulties arose during the determination of about 3×10^{-5}% of cadmium and indium.

The experimental setup used for evaporating the impurities has been described earlier [1]. Evaporation was carried out at atmospheric pressure, since on heating U_3O_8 in a vacuum, this oxide decomposes with formation of the more volatile uranium trioxide. Tests showed that during evaporation of cadmium oxide from the samples certain anomalies were observed. At a temperature of the graphite crucible of 1600-1700°, cadmium oxide evaporated intensively, and gave the impression that all the cadmium evaporated from the sample in the course of one minute, since repetition of the evaporation process at the given temperature did not lead to the deposition of cadmium on the electrode. Nevertheless, when the same sample of U_3O_8 was heated to a higher temperature (1900-2000°) cadmium was deposited on the electrode again. Spectrographic analysis of the condensate obtained by repeated evaporation at the higher temperature showed that the blackening of the spectrographic lines for cadmium was even greater than that obtained during analysis of the condensate obtained during the first minute of evaporation at a crucible temperature of about 1600°.

TABLE

Test element	Analytical line in A	Spectrograph used	Sample wt., in mg	Sensitivity in %
Cd	2265.02	ISP-22	200	$3 \cdot 10^{-5}$
In	4511.32	ISP-51	200	$3 \cdot 10^{-5}$
Ge	2651.17	ISP-22	200	$3 \cdot 10^{-5}$
Ga	2874.24	ISP-22	50	$3 \cdot 10^{-4}$
Au	2675.95	ISP-22	50	$3 \cdot 10^{-5}$
Sb	2311.47	ISP-22	200	$1 \cdot 10^{-3}$
Pb	4057.82	ISP-51	50	$3 \cdot 10^{-4}$

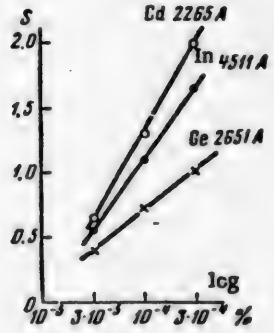
Thus, during evaporation of U_3O_8 samples containing cadmium as impurity, some processes occur which lead to partial combination of the cadmium in the sample. Accordingly, in order to avoid systematic errors it is essential to evaporate cadmium present as impurity at a temperature of about 2000°. This temperature is quite sufficient for ensuring that the oxides of all the other elements to be determined (In, Ge, Ga, Au, Sb, Pb) also evaporated, while it is still low enough to prevent appreciable evaporation of the U_3O_8 itself. In order to achieve the necessary degree

*For Communication 5 see Optics and Spectroscopy 3, 16 (1957).

of accuracy during determination of cadmium, indium, and antimony, 50 mg of U_3O_8 proved insufficient, and about 200 mg of the oxide had to be used. When a sample of this size was used the procedure adopted was to split it up into four lots of 50 mg, evaporating each lot of 50 mg separately and collecting all four condensates on one electrode; by following this technique the necessary increase in blackening of the spectrographic lines was achieved. This technique ensured the necessary sensitivity but it means of course that an analysis takes considerably longer.

Spectrographic analysis of the sublimate on the front surface of the electode was carried out using a condensed spark (generator IG-2; C = 0.012 μF; L = 0.15 mH). The inter-electrode distance was 2 mm. The accuracy of the electrode setting was established by means of a shadow projection. The most sensitive lines of the various test elements lie in various parts of the spectrum, accordingly it was found expedient to photograph the spectra simultaneously on two spectrographs (ISP-22 or Q-24 and ISP-51 with a focussing camera whose focal length was 270 mm). The analytical lines and some of the conditions used for carrying out spectrographic analysis of the sublimates are given in the Table.

In order to use the most sensitive line for indium – In I 4511.3 A – it was necessary to use silver electrodes, since on using copper electrodes, the intense copper line Cu 4509.5 A was superimposed on the analytical line for indium. In order to make use of the sensitive cadmium line Cd II 2265 A, photographing of the spectra in the ultraviolet was carried out on photographic plates "spectrographic, type III," which preserve their constrast and sensitivity in the far ultraviolet.



Calibration curves for the determination of Cd, Ge, and In in U_3O_8.

Analysis was carried out by the three-standards method. The standard mixtures were made up on the basis of pure samples of uranous-uranic oxide. The method of additions was also used for carrying out particularly important determinations. The mean square error for a single determination of any of the elements indicated did not exceed 15-20%, around the concentrations indicated in the Table. As an example, calibration curves for the determination of cadmium, indium, and germanium in uranous-uranic oxide are shown in the diagram.

The authors are indebted to A. N. Zaidel' for valuable advice and to G. G. Kuid for carrying out control tests.

SUMMARY

Cadmium and indium present as impurities in U_3O_8 do not volatilize completely when they are evaporated from the latter at 1600-1700°. In order to avoid systematic errors during the spectrographic determination of these two elements present as impurities in U_3O_8, it is necessary, therefore, to carry out evaporation at 2000°.

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Received February 7, 1957

*Original Russian pagination. See C.B. Translation.

POTENTIOMETRIC TITRATION OF BENZOQUINONE IN MALEIC ACID SOLUTIONS

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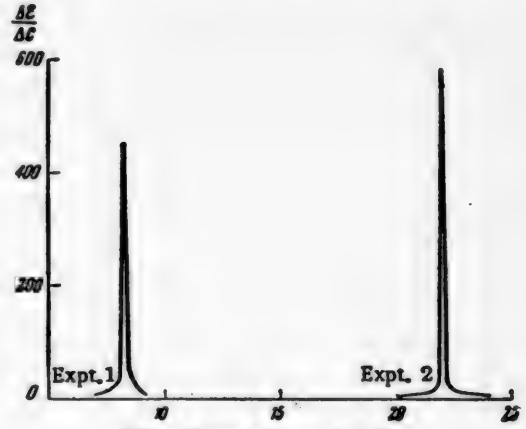
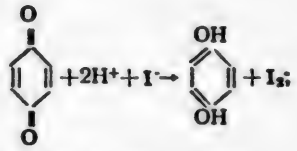
During the catalytic oxidation of benzene over a vanadium catalyst, in addition to the main reaction product – maleic acid – benzoquinone is also formed [1]; the quantitative determination of benzoquinone is of essential importance for the production control of maleic acid. Rzymkowski [2] tried to develop a reliable method of determining benzoquinone but he did not succeed in getting positive results.



For the potentiometric titration of the dark-orange colored solutions obtained, we used the usual iodometric method of determining benzoquinone [3].

1) 

2) $$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_2O_6^{2-}.$$

When this method was used a well-defined potential jump was observed and good results were obtained; a complete determination takes a few minutes.

Since a compensation scheme is regarded as being more reliable [4], we used an LP-5 potentiometer;

the redox potential of the system being titrated was measured by means of a platinum electrode with respect to the saturated calomel electrode.

For benzoquinone contents of the order of 0.0005 mole the experimental error did not exceed 3% relative.

The benzoquinone used for the experiments was synthesized from hydroquinone [5]. The melting point of the benzoquinone recrystallized from benzene and purified by sublimation under vacuum (5 mm Hg) was 112.0-112.5°. 30-40% aqueous production liquors of maleic acid and benzoquinone • obtained by catalytic oxidation of benzene over V_2O_5 [6] had a specific gravity of 1.106-1.137. 25-30% aqueous solutions of maleic acid were prepared from commercial maleic acid GOST 2806-51.

Benzoquinone was determined on a LP-5 laboratory potentiometer at 20-50°.

Experiment 1. 20.0 ml of the 40% production liquor of maleic acid, and 10 ml of 10% KI solution were taken. The liberated iodine was titrated from an automatic microburet with 0.1 N thiosulfate. The end point was established by the maximum $\Delta E/\Delta C$. The amount of benzoquinone was calculated on the basis that 1 ml of 0.1 N thiosulfate corresponds to 0.0054 g of benzoquinone.

The titration curve is shown in the diagram.

The end point was found at 8.24 ml which corresponds to 44.4 mg of benzoquinone.

Experiment 2. 20.0 ml of the same production liquor of maleic acid as that used in experiment No. 1 was taken; to this was added 76.2 mg of benzoquinone and 10 ml of 10% KI.

On titrations a total of 119.0 mg of benzoquinone was found. The difference between the first and second titration, amounted to 74.6 mg i.e. to 98% of the theoretical value. Similar results were obtained on adding various other amounts of benzoquinone. Formaldehyde does not affect the results during benzoquinone determination.

The electrode potential is rapidly established and 3-5 minutes are taken to carry out a titration.

Temp., in °C	$Na_2S_2O_3$ used up, in ml	Benzoquinone found, mg	% recovery of benzoquinone
47	3.90	42.2	105.5
44—48	3.85	41.7	104.3
44—50	3.77	40.7	101.8
20	4.07	44.0	110.0

Results for the direct potentiometric titration of benzoquinone with thiosulfate are given in the Table.

For each test 40 mg of benzoquinone and 20.0 ml of a 25% aqueous soulution of maleic acid were taken.

In this case 1 ml of 0.1 N $Na_2S_2O_3$ corresponds to 0.0108 g of benzoquinone. The electrode potential was only established slowly under these conditions, independently of the rate of addition of $Na_2S_2O_3$ and of the temperature. Direct titration of benzoquinone for any particular case cannot therefore be recommended.

SUMMARY

A method which is suggested for the determination of benzoquinone in maleic acid solutions is based on potentiometric titration with thiosulfate of the free iodine liberated during the interaction of potassium iodide with benzoquinone in acid media. Formaldehyde does not interfere.

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•The production liquor of maleic acid was extracted with benzene, as a result of which benzoquinone was isolated and identified.

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Received April 9, 1957

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CRITICISM AND BIBLIOGRAPHY

"Methods of Organic Chemistry," (Houben-Weyl) Fourth Completely Revised Edition. Editor E. Muller Vol. I, Part I. General Laboratory Practice. G. Time Press, Stutgart, 1958, pp. 1048.

The first part of the first volume of "Methods of Organic Chemistry," (General Laboratory Practice) edited by E. Muller, and published in January 1958, is the fourth edition, considerably enlarged and revised, of the well-known reference work of Houben-Weyl (the third edition was issued more than 20 years ago) in which a number of authors have participated, including O. Bayer, H. Meerwein, and K. Ziegler. 16 volumes will be published in the course of four years. The reference book will be devoted to questions of general laboratory practice, methods of organic analysis (Volume II), methods of preparing and the reactions of various classes of organic compounds, with special reference to high-molecular-weight compounds and various natural materials.

Volume I/I consists of 29 chapters containing valuable information on various materials used in the laboratory, and on methods of separating materials. A bibliography covering the literature up to 1955-1956 is included at the end of each chapter. Individual chapters (Glass apparatus connections, Ceramic masses, Repair of apparatus, Distillation and fractionation, etc.) are mainly of interest to the organic chemist. Some chapters contain information valuable for chemists working in other fields, particularly for the analytical chemist. In the chapter on the various types of glass for example, the chemical stability and physical properties of various makes of glass are described (e.g. glass for glass electrodes, light filters, etc.). In the chapter on metals and their alloys, tables are included illustrating the behavior of the metals and alloys used in the laboratory toward numerous chemical materials.

Measuring cylinders, crystallizing basins, water distillation apparatus, watch glasses, weighing bottles, beakers, etc. made from methacrylic ester polymers, polystyrene, polyamide, polyethylene, etc. and which are used in laboratory practice are described. Of interest for the analytical chemist is the replacement in certain cases of expensive platinum by polychlorotrifluoroethylene; e.g. during removal of H_2F_2 in silicate analysis (180°) it is possible to carry out evaporation in basins made from polychlorotrifluoroethylene mounted in aluminum; H_2F_2 can be stored in polyethylene vessels. Vessels which are capable of standing up to even aqua regia can be made from polytetrafluoroethylene.

Separate chapters are devoted to decantation and filtration, washing, clarifying and decolorization of solutions, and breaking up of emulsions. Purification of organic materials by making use of the formation of complex salts with the heavy metals (for hydroxy-acids, the hydroxyquinones of α-amino acids, oximes, diketones, bases, sulfamide preparations) is described. The theory and practice of extraction and partition are described separately. In the chapter on ion exchange, the basic characteristics of certain cation-and anion-exchange resins are described, as well as those of some resins used for special purposes (for catalysis, decolorization, sorption of oxygen). The use of ion-exchange chromatography for the determination of total electrolyte content, and for the removal of PO_4^{3-}, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$ is described; the study of complex formation, the preparation of pure reagents (for example, by passing H_2O_2 cooled to 0° through Wofatite, the stability of the former can be increased), determination of Cl^- in NaOH, preparation of standard NaOH solution by starting from NaCl and an anion-exchange resin in the OH^- form are also discussed.

A special chapter is devoted to redox resins, which are acquiring increasing importance.

The apparatus and application of dialysis, electrodialysis, and electrophoresis are considered.

The conditions required for drying materials are described. Volume I/I concludes with a discussion

of the planning and construction of a laboratory for organic chemistry.

On the whole this reference book is fairly complete, and the experimental techniques current in modern laboratories are fully discussed; theoretical questions are also included. Many of the chapters are of considerable interest to the analytical chemist.

V. G. Tiptsova

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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